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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
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MAR 14 1967
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Fall 1966

● VOLUME 9

● NUMBER 4

TECHNICAL PROGRESS REVIEWS

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The Atomic Energy Commission reluctantly announces that this is the final issue of *Reactor Fuel Processing*. This journal will be combined with the journal *Power Reactor Technology* beginning with Vol. 10, No. 1.

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Issued quarterly by the U. S. Atomic Energy Commission. Use of funds for printing this publication approved by the Director of the Bureau of the Budget on July 8, 1966.

To the Readers of *Reactor Fuel Processing*

With this issue *Reactor Fuel Processing* ends its existence as a separate journal. Beginning with the next issue (Vol. 10, No. 1) it will be combined with *Power Reactor Technology*, another member of AEC's family of Technical Progress Reviews.

I would like to express to the editors and to the Argonne staff members who have contributed to this journal the appreciation of the AEC for a job consistently well done. This journal has played an essential role through nine very active years which witnessed rapid developmental progress and the rise of private industrial enterprises in the fuel-processing field. We look forward to a continuation of this excellent work in the new combined journal.

Edward Brunenkant

Director
Division of Technical Information

Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

By W. J. Mecham and A. A. Jonke

Fuel-Processing Plans

Fuel-Reprocessing Plant Started Up in France

A major French fuel-reprocessing plant has gone into operation at La Hague, near Cherbourg.[1] The plant will handle only spent fuel from the EDF (Electricité de France) line of gas–graphite reactors at the outset. Other fuel types, however, can be accommodated by a simple adjustment at the decladding end of the line, according to the CEA (Commissariat à l'Énergie Atomique).

The plutonium yield through 1968 is earmarked almost entirely for military requirements, with breeder projects having next priority. No official disclosure was made of the plant's capacity, but authoritative sources have said that it will be up to 2 metric tons/day by 1970, with an expected doubling in the early 1970's.

First Privately Owned U. S. Processing Plant for Nuclear Fuel Starts Operation

The first privately owned nuclear fuel-reprocessing plant in the United States is now in operation. The plant, owned by Nuclear Fuel Services, Inc., was licensed to operate by the U. S. Atomic Energy Commission (AEC) on Apr. 20, 1966 (Ref. 2). Processing was begun immediately after licensing,[3] and the first shipment of processed fuel (in the form of uranyl nitrate solution) was made May 2, 1966 (Ref. 4). The plant has been described previously.[5,6]

Reload Fuel Supply for Dresden 1

A bid of about $8.5 million was accepted for a full reload core for Dresden 1 (Ref. 7). The core contains about 50 tons of slightly enriched uranium dioxide. United Nuclear Corp. bid successfully against other firms, among whom was General Electric Company, the designer and supplier of the reactor. The fuel is Dresden's type III-f, which is Zircaloy-clad, continuous-rod type, with removable burnable poison. The core will be loaded in five installments, a year apart, between 1968 and 1973.

Commonwealth Edison Co. also announced that it has arranged to buy between $15 million and $20 million worth of enriched UO_2 from United Nuclear. The material is to be delivered in the early 1970's for the fabrication of fuel for the Dresden 2 or 3 reactors.

AEC Completes Reexamination of Nuclear Fuel-Processing Technology

The AEC has recently completed a reexamination of its program for development of improved technology for the chemical processing of irradiated nuclear power-reactor fuels.[8] In this review the Commission held discussions in depth with representatives of potential chemical processors, reactor manufacturers, and power utilities concerning their plans and viewpoints and also reassessed the status of development of competition in the chemical processing industry.

As a result of this review, the Commission will continue its development program on the fluoride-volatility process. The fluoride-volatility process uses a different principle from the aqueous solvent-extraction processes now used extensively. Uranium and plutonium are separated from each other and are decontaminated from fission products by a process that utilizes the differences in volatilities of the hexafluoride compounds of uranium and plutonium and the fluorides of the fission-product elements. Industry has expressed considerable interest in the use of the fluoride-volatility process for future plants.

On the basis of information supplied by industry on plans to construct new chemical processing plants, the Commission considers that at the present time support in the form of a second base load of fuels, such as was furnished in establishing the first private plant, is not required to encourage the development of a competitive processing industry.

The Commission expects to continue the mutually advantageous exchange of information and comment on reactor fuel-processing programs. As part of its regular activities, the Commission promptly disseminates AEC technical information and offers programs providing work experience at AEC installations for industry personnel.[8]

New Contractor at NRTS

A new company, the Idaho Nuclear Corporation (INC) has taken over the contract for operation of the test reactors, the chemical processing facilities, the associated research and development, and the common support services at the National Reactor Testing Station (NRTS) in Idaho.[9] The new company is jointly owned by Aerojet-General Corp. and Allied Chemical Corp. The current level of the work is about $29 million per year and is contracted on a cost-plus-fixed-fee basis.

The new contractor was selected from several who had submitted proposals to the AEC last year, subsequent to the opening of the contract to competitive proposals. The competition was intended to enlarge the opportunities to nuclear firms and does not reflect any dissatisfaction with the previous contractor, the Phillips Petroleum Company. Phillips will continue as the AEC contractor for the extensive research and development program on reactor safety at NRTS.

Plans for Construction of a Fission-Products Conversion and Encapsulation Plant

The AEC has received an application from Isochem, Inc., for a permit to construct a fission-products conversion and encapsulation plant at the AEC's Hanford Works near Richland, Wash.[10]

The plant will recover the radioisotopes ^{90}Sr, ^{137}Cs, ^{147}Pm, and ^{144}Ce from waste products of the chemical processing facilities at Hanford and encapsulate these materials for sale, on a commercial basis, as sources of heat or radiation. This will be the first privately owned, large-scale commercial facility for processing and marketing of these fission products. Isochem's application estimates the cost of the facility to be in excess of $8 million.

Isochem is a subsidiary of U. S. Rubber Company and Martin Marietta Corp. Isochem currently is operating the Commission's chemical processing facilities at Hanford, under contract with the AEC.

Support Facilities at Hanford Available for Commercial Use

The Richland Operations Office of the AEC is seeking expressions of interest from federal and state agencies and from industry for in-place use of support facilities at the Hanford plant near Richland, Wash.

These facilities, located in two nuclear reactor production areas, have played an important role in national defense and have helped to open the expanding fields of nuclear technology. The areas contain two of the three reactors at Hanford which were shut down as a result of the Commission's decision in January 1964 to cut back the level of plutonium production.

The available facilities included in each area are four coal-fired steam boilers rated at 100,000 lb/hr; an electric-power-supply system, including a 230 kv/13.8 kv stepdown transformer, with a maximum rating of 31,250 kva each; pumping capacity of more than 80,000 gal of water per minute and a large water-filtering plant with chemical mixing facilities; approximately 200,000 sq ft of space suitable for manufacturing; 4-million-gal steel tanks (covered) and many other support facilities.[11]

AEC Seeks Industry Interest in Commercial Use of Weldon Spring Plant

Last April the AEC announced that the Weldon Spring plant would be shut down as part of a program to consolidate the feed-materials production operations at the Fernald plant near Cincinnati, Ohio, where the entire projected operation can be handled more economically. The shutdown of the plant is expected to be essentially completed by the end of calendar year 1966. As part of its policy to encourage development of a private, competitive nuclear industry, the Commission is sending letters of inquiry to a large number of industrial firms to determine the interest in private industrial utilization of the Weldon Spring plant for commercial atomic-energy activities, or for conducting such activities in combination with other nonnuclear industrial work.

The Weldon Spring facility is a complex located on about 200 acres of land and built at a cost of about $60 million. The facility has a capability of sampling bulk uranium-ore concentrates, refining uranium concentrates and recycling scrap, chemically converting purified uranium trioxide to uranium tetrafluoride, and producing massive uranium metal. The production output of the several processing units has varied from 8000 to 20,000 tons of purified uranium metal and compounds per year. Development and control laboratories and pilot-plant facilities are on site. Utilities and service facilities to support the production units and a plant population of 600 to 1200 employees are fully integrated into the complex. These include electricity, water, steam, propane gas, sewers, railroad spurs, fire protection, cafeteria, locker rooms, warehouses, administration and maintenance buildings, paved plant roads, and loading docks.[12]

Amendments Proposed for Regulations for U. S. Licensees for Fissionable Material

The AEC is proposing amendments to its regulations for licensees holding special nuclear (fissionable) material.[13] Previously, accountability for special nuclear material has been required in the contractual arrangements for the use of the government-owned material. However, under the private-ownership legislation approved on Aug. 26, 1964, special nuclear material in the future will not be subject to this mode of control. Therefore basic accountability requirements will be codified under licensing regulations. Processors and fabricators of nuclear fuel will be

required to furnish written descriptions of their accountability systems.

State Regulation of Radioactive Materials

The AEC has published for public comment agreements proposed by Alabama,[14] Louisiana,[15] and Nebraska,[16] under which the states would assume part of the AEC's regulatory authority over the use of radioactive materials. Under the proposed agreement the Commission would transfer to the individual states regulatory responsibility over the use of radioisotopes, the source materials uranium and thorium, and small quantities of fissionable materials.

Twelve states have already assumed this authority from the AEC: Arkansas, California, Florida, Kansas, Kentucky, Mississippi, New Hampshire, New York, North Carolina, Oregon, Tennessee, and Texas.

Program at ANL To Disseminate Technical Information to Industry

A new program to disseminate information to industry is being launched by the AEC at Argonne National Laboratory (ANL).[17] The purpose of the program is to identify technological innovations resulting from Argonne's research and development projects, to prepare brief, business-oriented summaries of these innovations, and to distribute the summaries to industry. The summaries will consist of descriptions of devices, processes, and techniques developed to meet specific scientific or engineering needs at Argonne. It is anticipated that many of the innovations, even though originated in connection with nuclear work, will be of interest to nonnuclear industry, including small businesses.

The summaries will be combined with similar information now published by the National Aeronautics and Space Administration (NASA). They will be known as the AEC–NASA Tech Briefs. The Briefs will be processed by NASA and distributed by the Clearinghouse for Federal Scientific and Technical Information, Springfield, Va., and through the eight NASA regional dissemination centers.

A Liquid Metals Information Center To Be Established

A Liquid Metals Information Center for gathering, evaluating, and disseminating material on liquid-metals technology has been established by the AEC at Canoga Park, Calif.[18] The Center will be operated by Atomics International, a division of North American Aviation, Inc.

The Center's major functions will be to respond to technical inquiries with answers based upon a critical evaluation of pertinent liquid-metal literature, to provide assistance to qualified visitors, and to maintain up-to-date data on current research and development in sodium and sodium–potassium technology. The Center also will produce a revised and expanded edition of the AEC *Liquid Metals Handbook*, last revised in 1955.

When totally operative, the Center will serve as a national information receiving and distribution point for use by government contractors and industry. It will be 1 of 19 specialized information centers for nuclear science and technology which are wholly or partially supported by the AEC.

Program Office Established by AEC for Liquid Metal Fast Breeder Reactor Development

The AEC has established a Liquid Metal Fast Breeder Reactor (LMFBR) Program Office at ANL.[19] The new office, reporting to the Director, ANL, will serve as an extension of the AEC's Division of Reactor Development and Technology to assist in the detailed planning, coordination, and evaluation of the many technical activities of the LMFBR program that will be carried out by AEC laboratories and industrial contractors. The office is functionally and administratively separate from research and development activities of the Laboratory.

The Program Office is composed of a number of special suboffices, each headed by a full-time senior scientist or engineer, reporting to a Program Office Director. These suboffices will be responsible for specific major elements of the fast breeder development program which include plant design, fuels and cladding materials, fuel reprocessing and recycling, sodium technology, components, instrumentation and controls, physics, and safety.

International Review of Status of Programs for the Use of Plutonium in Power Reactors

The International Atomic Energy Agency (IAEA) convened a panel of experts in Vienna on Dec. 7 to 11, 1964, to review, on an international basis, the current information on various aspects of plutonium utilization, including physics of plutonium, the technology of plutonium fuels in thermal and fast reactors, the behavior of plutonium fuel under reactor irradiation, and technological and economic aspects of plutonium fuel cycles. The published report of the panel contains 12 status reports by participants from Belgium, Canada, France, Germany, India, Italy, Japan, the United Kingdom, and the United States. Summaries of the status reports and panel discussions are presented under seven technical topics. This comprehensive international review volume is the accomplishment of 23 participants.[20]

Economics of the Fuel Cycle

Upswing Forecast in Commercial Uranium Market

The commercial market in uranium is expected to take an upturn in 1972 as a result of increased nu-

clear power generation.[21] Commitments were made for nuclear plants having a capacity of 5000 Mw(e) in 1965 and an additional 7200 Mw(e) in the first half of 1966. A recent estimate of installed capacity is 12,200 Mw(e) by 1970 and 94,000 Mw(e) by 1980. On the basis of expected reactor performance, a forecast has been made of the U_3O_8 ore requirements as shown in Fig. I-1.

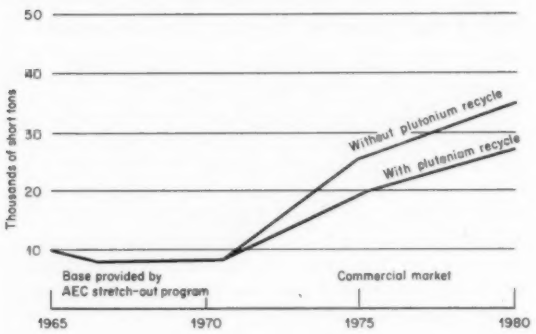

Fig. I-1 Estimated U. S. requirements of U_3O_8 (Ref. 21). Reprinted here by permission of Chemical and Engineering News, *44(27): 18 (July 4, 1966).*

The increased rate of nuclear power plant construction has been attributed to the increasingly favorable competitive position of nuclear plants with respect to fossil-fueled plants, a position which is due principally to reductions in capital costs of nuclear plants and increases in capital cost of fossil plants. It was reported that in Northern Illinois the nuclear units of the 800-Mw(e) class enjoy a 10% cost advantage over coal-fired plants. Among the newly projected nuclear plants are multireactor units of more than 2000 Mw(e) total power.

The commercially competitive reactors are cooled and moderated with natural water (boiling or pressurized) and are fueled with UO_2 enriched to about 3.0% ^{235}U. The enrichment process requires 4 to 6 tons of natural uranium to produce 1 ton of enriched reactor fuel. Natural uranium in the amount of about 1 ton per installed electrical megawatt is required for reactor fuel inventory, with an additional amount of the order of 0.2 ton required per megawatt-year of operation. For the projected nuclear economy, annual requirements of natural uranium have been estimated at more than 7000 tons of U_3O_8 by 1970 and 27,000 to 35,000 tons by 1980.

The U. S. uranium-enriching facilities are operated under the AEC and will enrich domestically owned uranium for use in U. S. reactors. Natural uranium contains 0.71% ^{235}U, the balance of natural uranium being chiefly the isotope ^{238}U.

Fissionable plutonium is produced as a by-product in nuclear reactors. At present the AEC allows a buy-back price of $10 per gram of fissionable plutonium as recovered from spent-fuel-reprocessing operations, but this buy-back credit will not be available after Jan. 1, 1971. However, the industry-owned plutonium can be used to reduce part of the enriched-uranium-fuel requirements.[21] (Another possible commercial use of utility-owned plutonium is to fuel fast reactors, which can fission the large amounts of ^{238}U in depleted uranium that is an interim loss from the isotope separation plants.)

Commercial Orders for Enriched Uranium

Statistics on the major commercial and foreign orders for U. S. enriched uranium are now presented in *Nucleonics*. The data comprise enriched-uranium orders for use as a nuclear fuel in commercial electric-power generation; they do not include orders either for military or for research quantities.[22]

AEC Enrichment Services

The AEC has published draft contracts for the furnishing of uranium-enrichment services. Under the Private Ownership of Special Nuclear Materials Act of 1964, the AEC is authorized to enter into long-term contracts for the receipt of privately owned uranium, its enrichment in the fissionable uranium isotope 235, and return of the enriched uranium to the customer of the enrichment service for a fee. This toll enrichment service can be accomplished at the AEC's three large gaseous diffusion plants in Oak Ridge, Tenn., Paducah, Ky., and Portsmouth, Ohio, after Dec. 31, 1968.

The private-ownership act requires the AEC to submit to the Joint Congressional Committee on Atomic Energy its criteria for the furnishing of this service. Copies of both the criteria and the contracts may be obtained on request from Joseph L. Smith, Director, Division of Contracts, U. S. Atomic Energy Commission, Washington, D. C. 20545 (Ref. 23).

Charges are being reduced for handling and packaging of enriched uranium from AEC gaseous diffusion plants. This will result in a savings to the nuclear power-reactor operators who use uranium enriched in the fissionable isotope ^{235}U for reactor fuel.[24]

It is estimated that in the next few months orders will amount to as much as 100,000 kg.

Because of improvements in the procedures for withdrawing uranium hexafluoride, in the form of a gas, from the diffusion plants, it is possible, for example, to reduce the charge to about $.4500 on a 12,000-kg shipment that previously would have cost $7400 in handling and packaging charges.

This drop in cost is due to the elimination of much of the sampling and analysis work to determine the enrichment level of each shipment. The material, which previously was sampled in small lots, now may be drawn into one large cylinder, up to 10 tons in

size. One sample is taken, and then the material is transferred into smaller containers for shipment.

The new schedule of charges was published in the *Federal Register* on Tuesday, Apr. 5, 1966, and became effective immediately.[24]

The question of whether U. S. enrichment capacity was adequate to meet coming demands of nuclear power was discussed by AEC Chairman Glenn T. Seaborg before a meeting of the National Association of Manufacturers. "Present U. S. gaseous diffusion plants have sufficient capacity for the continuing requirements of more than 100,000,000 kilowatts of installed civilian nuclear generating plants ... during the latter part of the 1970's it probably will be necessary to begin the construction of new enrichment facilities ... our continuing advances in enrichment technology promise that these new plants can be economically built and cause no change in the cost of separative work required to enrich the uranium."

The present diffusion plants are government owned and operated; alternative arrangements are to be considered for any new plants.

Dr. Seaborg presented the most recent AEC projections of commercial nuclear power generation; he said that "by 1970-71 there will be more than 10,000,000 kilowatts of nuclear electric generating capacity in the U. S., and by 1980 there will be between 80,000,000 and 110,000,000 kilowatts."

About the projected growth of civilian nuclear power abroad, Dr. Seaborg said that it "is as impressive as that here at home. In fact, at this point in time, the UK leads the U. S. in total installed nuclear capacity. Forecasts made recently indicate that by 1970 more than 4,000,000 kilowatts of nuclear generating capacity, fueled with U. S. slightly enriched uranium, will be installed abroad. At the same time, in 1970, the nuclear generating capacity abroad fueled with natural uranium should be about 10,000,000 kilowatts. These figures can be compared with the U. S. total projected capacity of about 10,000,000 kilowatts in about the same time frame. By 1980, it is estimated that there will be in operation abroad from 70,000,000 to 100,000,000 kilowatts of nuclear generating capacity fueled with U. S. slightly enriched uranium. In addition, there should be about half this capacity or approximately 40,000,000 kilowatts of nuclear generating capacity fueled with natural uranium. Comparing these figures with the U. S. market estimated for 1980 — 80,000,000 to 110,000,000 kilowatts — it is apparent that the growth abroad will be quite similar to that in the United States."[25]

Diffusion-plant capacities and costs have been previously estimated unofficially by several authors.[26-28]

Commercial Plutonium Fuel Conference

A preliminary account of the Commercial Plutonium Fuel Conference, Mar. 1–2, 1966, in Washington, D. C., was reviewed from news sources in the previous issue of *Reactor Fuel Processing*. This review dealt principally with plans of private industrial firms for fuel testing programs. The larger scope of the Conference, including AEC programs and consideration of the plutonium utilization in the nuclear economy as a whole, is reviewed here from the recently published volume of papers and discussions presented at the Conference.[29]

The AEC position was presented in statements by Ernest B. Tremmel, Director of the Division of Industrial Participation; Milton Shaw, Director of the Division of Reactor Development and Technology; and F. P. Baranowski, Director of the Division of Production. At the outset of the Conference, the private ownership of nuclear fuel appeared as the key condition under which the technical issues of plutonium utilization were discussed. With financial responsibility for plutonium generated in power reactors resting with the utilities, AEC spokesmen expressed a sense of urgency in promoting the industrial technology necessary to serve the needs of the utilities. The two technical alternatives for utilization of plutonium generated in power reactors are (1) recycling the plutonium (which allows reduction of the uranium requirements of thermal power reactors by up to 40%) and (2) using the plutonium fuel in fast breeder reactors (which are capable of operation with about $\frac{1}{40}$ of the uranium requirement of thermal reactors). Indications are that financial needs of utilities will require both of these options in the future. An economic balance is expected to determine the fraction of plutonium recycled and the fraction reserved for starting fast reactors.[29]

Utilization of plutonium requires a fuel-processing and fabrication capability as well as a reactor capability. In order to provide an early industrial base, the AEC will obtain some of its own research and development plutonium requirements from industrial suppliers, even though the AEC has its own fabrication facilities.[29]

British and Canadian spokesmen contributed their views to the Conference discussion. N. L. Franklin of the Production Group of the U. K. Atomic Energy Authority stated the U. K. position succinctly:

> 1. The 5000 Mw(e) of magnox reactors operating or under construction in the U. K. will produce about 2½ tonnes of fissile plutonium per year from 1970 onwards.
> 2. The Advanced Gas Cooled reactors which will form all, or most, of the 8000 Mw(e) to be brought on power between 1970 and 1975 can be plutonium fueled, but even the U.K. supplies are not adequate for this purpose — some A.G.R.'s will have to have ^{235}U enrichment.
> 3. The U.K. will be producing its own enriched uranium at prices which, based on nuclear power electricity, will be in the same ball park as the U. S. separative work costs.
> 4. The prototype fast reactor of 260 Mw(e) for the construction of which Government approval has now been given, will be on power in 1970-1971.

Two further assertions were made about economics:

1. That the price of natural uranium will go up rather than down, even when a successful fast reactor can be constructed.
2. That such a fast reactor will have an appreciably better economy for high load factor operation than the available thermal reactors at the then prevailing uranium prices.[29]

Recycle of plutonium in thermal reactors is not a part of the British program. The British plan to recover and store the plutonium from thermal power reactors, and the stocks of plutonium will be used for the startup of fast reactors when economically advantageous. This plan was said to be based on a system analysis in which introduction of commercial fast reactors was assumed to occur in 1971 and in which the cost of money was 8%/year. On the other hand, a doubling of the cost of money and a delay of, say, 7 years in the introduction of commercial fast reactor operation, would have given a result in favor of recycle rather than storage of all of the plutonium.[29]

Use of plutonium in the Canadian reactor program was described by J. L. Gray of Atomic Energy of Canada Ltd. The heavy-water-moderated natural-uranium-fueled reactor is considered to be economical in Canada without obtaining any credit for plutonium in spent fuel. Although the possibilities of value of the plutonium is not denied, the present value of plutonium is set at zero because there is not an actual market for the plutonium in its present form. Canada now has heavy-water plants and ample uranium resources but no spent-fuel-processing facilities. The Canadian decision accordingly has been made to store the plutonium until suitable markets develop.[29]

Industrial fabrication of plutonium fuel was discussed by representatives of several U. S. firms. The Babcock & Wilcox Co.'s Nuclear Development Center in Lynchburg, Va., is designed primarily for the development and testing of fuel elements containing plutonium and ^{233}U, according to the statement presented by M. C. Edlund. The Center's several laboratories are equipped for work in the areas of (1) experimental reactor physics, (2) feed-materials process development, (3) fuel-element fabrication and assembly development, and (4) irradiation testing of materials and fuel assemblies. The laboratory includes a 1-Mw pool type research reactor and the Babcock & Wilcox test reactor. Equipment is provided for various types of ceramic fuel-element preparation, but emphasis at the Center has been placed on the development of high-density mixed oxides (PuO_2 and UO_2) prepared by the sol-gel method and fabricated into fuel elements by vibratory compaction. Glove boxes are used for alpha containment in the feed material and fabrication operations. Remote cells are available when higher levels of radiation are encountered.[29]

Nuclear Fuel Services, Inc., has a spent-fuel-reprocessing plant at West Valley, N. Y., and a plant at Erwin, Tenn., for fabricating fuel rods in the form of UO_2-PuO_2 pellets. The fabrication plant was described by E. R. Johnson as being capable of supplying production quantities of mixed oxides. Other plutonium capabilities are planned, and plant capacity can be readily expanded. At present the fabrication plant is producing 2000 kg of UO_2-PuO_2 fuel pellets for a Savannah River experiment.[29]

At Atomics International, interests are directed entirely toward fast breeders, and requirements for processing and fabrication facilities are being planned. As described in a statement by Harry Pearlman, emphasis at Atomics International is placed on refractory fuels, with carbides and possibly nitrides considered the most promising. In its present form the 9600-sq ft facility is designed for flexibility and has an expected cost of close to $1 million.[29]

The Nuclear Materials and Equipment Corporation (NUMEC) at Apollo, Pa., is operating a pilot-scale plutonium-fuel-fabrication complex. Currently, alloy and oxide fuels containing plutonium can be supplied at the rate of 1000 kg of contained plutonium per year. The complex is flexible and provides for supporting research and development. The investment, as cited in the statement by Karl H. Puechl, amounts to $6 million.[29]

A statement by William F. Roche described the plans of the United Nuclear Corp. United Nuclear and Douglas Aircraft are to establish a plutonium-fuel-fabrication facility at Hanford, Wash. The initial plant line will be capable of handling a capacity of 60,000 kg of mixed oxides per year with designed expansion to 400,000 kg/year. The new facility will be directed mainly at recycle fuel for thermal power reactors but will have versatility for other types of plutonium-containing fuels. The plant will be capable of producing vibratory-compacted as well as sintered pellet fuel. The plant will also have all the necessary equipment for finishing the tube element bundle, including autoclaving, if required. The plant will be capable of handling both zirconium and stainless-steel cladding.[29]

The United Nuclear Corp. now makes plutonium-fuel compounds in its research laboratories in Pawling, N. Y. The laboratories were built 7 years ago and have been continually in operation since that time, developing fuel materials for the fast breeder program, principally mixed uranium–plutonium carbides. Many of the glove boxes are operated with a high-purity inert-gas atmosphere. Under the sponsorship of the AEC, a powder-metallurgy process for making uranium–plutonium carbide fuel has been developed by United Nuclear and its subcontractor, the Carborundum Co.[29]

The effect of timing of commercial approaches to reactor and fuel fabrication was discussed, respectively, in statements by E. L. Zebroski of General Electric Company and Karl H. Puechl of NUMEC. Zebroski reviewed the status of fast reactors. The United States, Britain, and Russia each have one operating pilot-scale fast reactor. There are 13 committed and planned units in Europe. In the United States there are 3 units operating or under construction and 3 or 4 more in the planning stage. With

favorable results from present development programs, normal competitive forces would be expected to make desirable the U. S. commitment of 300-Mw(e) fast reactor units, which would correspond to the intermediate-sized operation of thermal reactors such as Dresden and Yankee.[29]

In a discussion of plutonium requirements and availability for fast reactors in the future, Zebroski estimates that the minimum U. S. fast reactor program will consume over half of the available plutonium. An accelerated program could easily lead to a plutonium-limited condition in the late seventies. A balance between thermal recycle and accumulation of plutonium for fast reactors will have to be achieved, since short-term unbalances would no doubt exist between plutonium supply and demand.[29]

The possibility of long-term plutonium difficulties was discounted by Zebroski on the grounds that fast reactor development allows considerable flexibility with respect to the key design parameters (breeding ratio and specific power) which determine plutonium purchase requirements in a nuclear economy. Zebroski[29] cited the figure of merit for new inventory requirements as

$$I = \frac{K_1}{p^2 b}$$

where I = fissile inventory required, kg/Mw-year
p = system specific power, Mw/kg
b = excess breeding gain, kg/Mw-year
K_1 = a dimensionless constant

Presumably, this figure of merit was derived from an assumption of a linear increase rate of total fast reactor power with time. Such a linear power–time relation was the basis of a similar figure of merit presented by Young in a 1964 paper.[30] In derivation of such factors of merit, alternative assumptions of fast reactor growth can give different results. For example, Kasten in a 1965 statement[31] recommended a growth rate of the form in which power is directly proportional to the square of the time in years from a startup time. For this case the figure of merit was equivalent to

$$I = \frac{K_2}{p^3 b^2}$$

where K_2 is a dimensional constant. The inclusion of doubling time in both the above formulas may be seen by noting that doubling time is inversely proportional to the product of specific power p and breeding ratio b.

In the very early stages of fast reactor power, when fast reactors produce only a small fraction of total nuclear power, plutonium for new fast reactors can be obtained from thermal reactors, and under these conditions the breeding ratio is of minor significance for fast reactor growth. In a fully developed fast reactor economy, when fast reactor power predominates, further growth requires that the plutonium doubling time from fast reactors be only slightly different from the total growth of power capacity. The interim period, say, from 1980 to about 2000, may be the time in which breeding ratio and doubling time are most significant. Zebroski considers that the demonstration of safety and economic power generation in early fast reactors would allow fast reactors to capture a share of the power economy. Subsequently, adjustment of reactor parameters would be able to achieve minimum overall power costs in conjunction with thermal reactors.[29]

The larger economic picture includes uranium ore and enrichment costs, but these costs were not considered at the Conference.

Large-scale fuel facilities (>5 tons of plutonium per year) are not expected to be required until after 1975. The relatively high cost currently associated with plutonium-fuel fabrication is associated with low production rates. Since the value of plutonium for thermal recycle is equal to the ^{235}U which it replaces less the added cost of fabrication and handling of plutonium, the net value of plutonium for plutonium-recycle purposes may in the near future be lower than its potential value at future, high production rates.[29]

The relation of fabrication cost of plutonium fuel to production rate was discussed in more detail by Puechl of NUMEC. A cost breakdown of the fabrication of fuel elements containing 1000 kg of plutonium is shown in Table I-1. The unit cost of $5000 per kilogram of plutonium is currently representative of costs for mixed oxides and other fuels containing more than 5% plutonium. Cost reductions are expected chiefly through automation, which would be appropriate for a production rate of about a ton of mixed oxides per day, which is, of course, much higher than present demand for mixed oxides. Until more automation is employed, it appears that the cost of plutonium fabrication will be substantially higher than that for pure uranium.[29]

Table I-1 COST BREAKDOWN FOR FABRICATION OF FUEL ELEMENTS CONTAINING 1000 kg OF PLUTONIUM

Item	Millions of dollars	Percent of total
Processing and fabrication	1.20	24
Analytical chemistry and quality control	0.62	12
Use charges (500 kg for 1 year; $40/g Pu at 4.75% interest per year)	0.95	19
Insurance	0.15	3
Withdrawal, handling, analyses, and shipping charges	0.40	8
Shipper-receiver difference	0.08	2
Processing losses at 2%	0.80	16
Scrap recovery and recycle	0.80	16
Total cost	5.00	100

World Competition in the Nuclear Industry

Differences among nations as to their nuclear industries enter into competition in the world market.

A recent assessment has been made by the staff of *Nucleonics*[32] of the capabilities of seven European nations and Canada in the area of reactor manufacturing and fuel supply. The eight nations reported on — Belgium, Britain, Canada, France, Germany, Italy, Sweden, and Switzerland — are expected to be included among the most significant participants in the growing world market for nuclear power. Although all of these nations are entering the world market, the largest efforts seem to be those of Britain and Germany.

Britain, which has more installed nuclear power than any other country by a wide margin, plans to step up its foreign marketing activities in an effort to win export orders for its new Advanced Gas Cooled Reactor (AGR) as well as for the fuel supply and reprocessing services of the U. K. Atomic Energy Authority. For this purpose a foreign marketing agency has been created, the British Nuclear Export Executive (NBX). In Britain the Atomic Energy Authority (AEA) is the sole developer of reactor technology and the owner–operator of national fuel facilities; reactors are built by three industry consortia.[32]

The AEA fuel-fabrication facilities at Springfields can turn out 2500 metric tons of magnox (natural uranium metal) fuel elements per year. Present small-scale oxide-fuel fabrication will be increased to 150 metric tons/year in less than 2 years. Fast breeder fuel production lines are also programmed for Britain's fast breeder prototype.[32]

At Windscale the AEA has a reprocessing plant capable of handling 2000 metric tons of the uranium metal fuel per year and is being modified to include 300 metric tons of oxide-fuel-handling capacity per year. Reprocessing costs of $8400 per metric ton for metal fuel and $14,000 per metric ton of oxide fuel were reported, on an unsubsidized basis. (These figures do not include fuel transportation costs, or, presumably, any final conversion costs for the fuel material.)

Plutonium and enriched uranium are included in fuel-cycle services offered. Plutonium credit of $5.6/g on an all-isotopes basis was assigned to the AGR reactor at the Dungeness B power station. Plutonium buy-back also may be included in AEA reprocessing or fuel-cycle services. The diffusion plant at Capenhurst is being modernized to improve competitive position.

In Germany, reactor manufacturing is done by two highly self-sufficient electrical equipment firms, AEG (Allgemeine Elektricitaets Gesellschaft) and Siemens. These companies are licensees of the U. S. firms General Electric and Westinghouse, respectively. The firms AEG and Siemens are offering nuclear plants in the current bidding in the European market.[32]

The German firm NUKEM is a major fuel supplier, jointly owned by several industrial companies. Together with its subsidiaries, NUKEM has capability for chemical conversion and fabrication for complete fuel assemblies of uranium or plutonium. It also offers service contracts for shipment of spent fuel for reprocessing in other countries.[32]

Although the German government has appropriated $15 million for construction of a fuel-reprocessing pilot plant of 40 tons/year capacity, Germany is not expected to be a competitor in the foreign fuel-reprocessing business in the near future.[32]

Community Attitudes Toward Nuclear Installations

One aspect of the selection of sites for nuclear installations of various types is the response of the public. In order to aid in evaluating this factor, a recent survey[33] was made of attitudes about locating nuclear reactors in the community. The survey was sponsored (anonymously) by the Babcock & Wilcox Co. and was designed and conducted with the cooperation and approval of the Consolidated Edison Co., for whom Babcock & Wilcox built the reactor at the Indian Point power plant near Buchanan, N. Y. Professional field interviewers carried out the survey among residents of three cities with varying experience with atomic reactors. The cities were (1) Buchanan, N. Y., where the Indian Point reactor has been operating for some time; (2) Philadelphia, Pa., where public discussion has recently been conducted about obtaining a nuclear reactor; and (3) Atlanta, Ga., where there is no reactor nor has there been contemplation of one. Besides the city of residence, other factors against which attitudes were correlated were age, sex, and education.[33]

In such a survey a simple characterization of personal response is difficult. A respondent can be enthusiastic in his support of nuclear-electric power but, at the same time, critical of his experience with it. Or he may admit to a complete lack of knowledge about it but be certain he wants no part of it. Also, an appreciable fraction of responses were simply noncommittal (women were on the average more noncommittal than men).[33]

In general, the survey found that residents who were more familiar with nuclear-electric power were more favorably disposed toward it. Buchanan residents were more favorable than those of either Philadelphia or Atlanta. Also, residents of Philadelphia, where there has been more public education on nuclear power, had more favorable responses than residents of Atlanta. Some observations were made as follows: men tended to be more favorable toward nuclear plants than women; younger people more favorable than older; college trained more favorable than less educated. However, individual exceptions were found to all attempted correlations. Four basic questions were:

1. What is your overall impression of nuclear energy for the production of electricity for the home?
2. How "clean" are nuclear plants in operation?
3. How safe are nuclear plants to work in?
4. How safe are communities in which nuclear plants are located?[33]

In the latter question on community safety, 3% of Buchanan respondents considered their community's safety at least somewhat impaired by the presence of a nuclear power plant. In Philadelphia and Atlanta this negative expression of concern was about 15%. On this question the age and sex effect mentioned above was observed, but educational attainment was apparently not a factor.[33]

In response to a question applicable only to Buchanan, more than 75% of the residents of that nuclear power community said they prefer their nuclear plant to a conventional plant; only 6% expressed preference for a conventional power plant.

Babcock & Wilcox believes that the study has once again confirmed the need for public education on the subject of nuclear power. To be effective in reaching women and older people in the community, however, methods different from the usual ones (such as newspapers) may have to be found.[33] The published account, however, did not discuss specifically the state of public education in Buchanan.

Patents Available for Public Use

The AEC has made available for public use 45 Commission-owned French patents,[34,35] and 68 U. S. patents.[36,37] The Commission will grant nonexclusive royalty-free licenses on the listed patents as part of its program to make nonsecret technological information generally available for use by industry. To date, 3677 patents and applications have been so released by the AEC.

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Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

Dissolution of ThO_2-UO_2 in HNO_3 and of Zircaloy in NH_4F–citric acid is reviewed. The feasibility of elutriating ash from burning graphite-matrix fuels in a fluid bed is discussed. Further work on extraction of RuNO complexes is presented, along with information on radiation-damage effects in amine solvent systems. A review of simple, low-decontamination aqueous process steps applicable to close-coupled plants indicated little potentiality for operations other than solvent extraction. Application of mixer–settlers to thorium extraction is considered, and a correlation of pulse-column flooding data is presented.

Preparation for Fuel Processing

By C. E. Stevenson

The chief factors affecting the rate at which ThO_2-UO_2 dissolves in HNO_3 are acidity, temperature, and cationic (Al^{3+}, Zr^{4+}, Be^{2+}) and anionic (F^-, SO_4^{2-}) additives. Zircaloy may be dissolved in an NH_4F–citric acid reagent. Fluoboric acid may be added in HF processing of zirconium fuels as a nuclear poison with little effect on the process. Alloys of molybdenum and uranium may be decomposed in alkaline melts. Most of the ash resulting from burning graphite-matrix fuels in a fluidized Al_2O_3 bed is readily elutriated from the bed.

Dissolution of Urania–Thoria Fuel Particles

In a high-temperature gas-cooled reactor (HTGCR) concept, which is being developed by the Australian Atomic Energy Commission, the use of a dispersion type fuel with a beryllia matrix containing particles of UO_2 in solid solution in ThO_2 is proposed.[1] The fuel cycle proposed consists in grinding the fuel to permit leaching of the UO_2-ThO_2 from BeO with HNO_3, followed by dissolution of the residue in H_2SO_4 to allow recovery of BeO, as shown in Fig. II-1. Farrell and Isaacs have recently described studies of dissolution rates of UO_2-ThO_2 fuel particles,[2] as might be used in the fuel matrix of such a reactor.

The −72 +100 BSS* particles containing 5% UO_2 in ThO_2 were prepared by wet ball-milling together finely ground ThO_2 and UO_2 particles; then pelleting, pressing, crushing, screening, and sintering the material (2 hr at 1700°C in hydrogen). Total dissolution in $13M$ $HNO_3-0.001M$ F^- required more than 3 hr at 115°C, as was observed earlier in work at Oak Ridge National Laboratory (ORNL).[3] The effects of varying reagent composition and temperature were evaluated by comparing the initial slopes of the dissolution-rate curves. Since by itself UO_2 generally dissolves much more rapidly than ThO_2, it was assumed that its dissolution was proportional to that of ThO_2.

In the range $8M$ to $13M$ HNO_3, with $0.05M$ F^- at 115°C, the initial dissolution rate was first order with respect to HNO_3 concentration and fell off at higher concentrations. In $13.4M$ acid, 51 mg of ThO_2 dissolved per minute per gram of ThO_2 present. A small amount of fluoride ($0.001M$) is very effective in promoting ThO_2 dissolution; in the range $0.001M$ to $0.05M$ F^-, the rate increased from 10 to 47 mg/(g)(min), equivalent to about one-half order reaction. The temperature effect (with $13M$ $HNO_3-0.05M$ F^-) in the range 70 to 130°C corresponded to an activation energy of 19 kcal/mole, or approximately a doubled rate for each 10°C increase.

The effects of cationic additives on the rate of dissolution were also studied. These included beryllium, zirconium, and aluminum, since beryllia is the major constituent of the fuel matrix, zirconium may be considered for use in constructing the leaching vessel, and $Al(NO_3)_3$ is frequently added to fluoride-bearing HNO_3 as an inhibitor of the corrosion of stainless steel. As shown in a semilog plot in Fig. II-2, all three metals inhibit the dissolution of ThO_2 but are of widely differing effectiveness. The order of decreasing effectiveness is $Zr^{4+} > Th^{4+} > Al^{3+}$ and is the same as that of the stabilities of the simplest fluorocomplexes of these metals of the type MF^{m+}. Another significant chemical effect on the dissolution rate was found to be that of SO_4^{2-}: $0.02M$

*British sieve series.

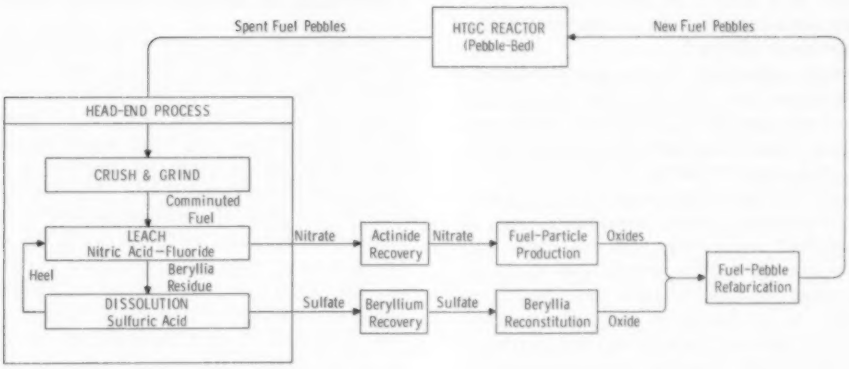

Fig. II-1 Fuel cycle for HTGCR using a beryllia-based dispersion type fuel.[2]

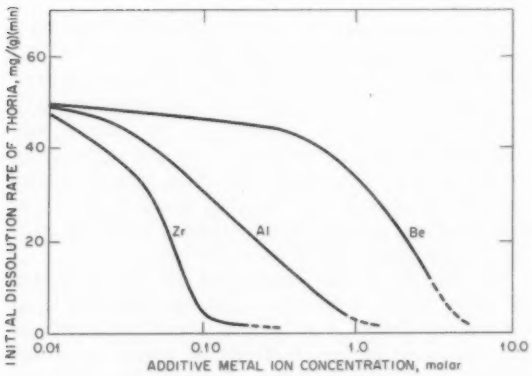

Fig. II-2 Comparative effect of beryllium, aluminum, and zirconium on the initial dissolution rate of thoria[2] *in 13M HNO_3–0.05M F^- at 115°C.*

SO_4^{2-} effected a fivefold reduction in the dissolution rate with 13*M* HNO_3–0.05*M* F^- at 115°C. The rate was further reduced with 0.2*M* SO_4^{2-}. This is significant in that it is proposed to dissolve BeO in H_2SO_4 and to return undissolved residue to HNO_3 leaching.

Dissolution of Zircaloy

Uranium dioxide fuel elements clad with zirconium or Zircaloy may be dejacketed by dissolving the cladding in boiling 5*M* to 6*M* NH_4F–0.5*M* to 1.0*M* NH_4NO_3 (Ref. 4). Average dissolution rates with a fluorine-to-zirconium ratio of 7 are 10 to 15 mils/hr for unoxidized Zircaloy but are only 20 to 30% of this value for cladding that has been exposed to water at a high temperature. The dissolving reaction liberates hydrogen and NH_3; the presence of NH_4NO_3 minimizes hydrogen production, and NH_3 is removed by steam sparging or boiling without reflux. Dissolution is slowed if NH_3 is not removed. Some attack on UO_2 occurs in the course of the dissolution.[5]

Marchant and Van Caeneghem of the Eurochemic plant at Mol, Belgium, have proposed a modification of this decladding process in which less concentrated (3*M*) NH_4F, containing 2.5*M* citric acid, is used as the dissolving reagent.[6] No NH_4NO_3 is used. It is stated that ammonia removal is not necessary with this reagent. Hydrogen is formed in an amount stoichiometrically equivalent to the amount of zirconium oxidized, but this is not felt to be a problem in the absence of the necessity for NH_3 removal to maintain an adequate dissolution rate. Dissolving rates are of the order of 2 mg of zirconium per square centimeter per minute, and oxidized material dissolves more slowly than clean metal.

Final stable solutions with zirconium concentrations as high as 1.5*M* are obtainable (0.1*M* with oxidized material), which is significantly higher than the zirconium concentration normally achieved in NH_4F–NH_4NO_3 dissolution [a final fluorine-to-zirconium ratio less than 7 is recommended for the latter to avoid formation of less soluble $(NH_4)_3ZrF_7$]. This lessens the volume of cladding waste. It is noted also that the citric acid reagent dissolves considerably less powder or pelleted UO_2 than does 6*M* NH_4F–1*M* NH_4NO_3. There is some radiation effect on citric acid, since a capsule of 2.7*N* acid exposed to 10^9 rads (^{60}Co) decreased in acidity to 2.3*N*.

The zirconium compounds formed in dissolution have not been isolated, and their nature is not well understood. It is thought that decomposition of alkaline fluorides by the organic acids liberates HF, which oxidizes zirconium to Zr^{4+}, and that soluble zirconium complexes are formed which comprise both fluorine and an organic radical. An NaF–citric acid dissolving mixture was also studied, but the low solubility of NaF (0.9*M*) limits the achievable zirconium concentration and the average dissolving rate. Further, insoluble NaF·HF is formed, and oxidized zirconium is practically nonreactive.

With the NH_4F–citric acid reagent, tin present in Zircaloy-2 is not dissolved and remains as small

metal particles. If a nitrate is added (about 0.7*M*), the tin may be dissolved, but the zirconium dissolution rate is adversely affected.

It was recently reported[7] that a semicontinuous dissolution process for Zircaloy-clad zirconium–uranium alloy fuels had been placed into successful operation at the Idaho Chemical Processing Plant (ICPP). This was a modification of the older batch HF dissolution, $Al(NO_3)_3$ complexing, tributyl phosphate (TBP) extraction process previously used, in which the dissolver utilization was markedly improved by the use of soluble poison (boron) in the dissolving reagent of appropriately modified composition, which is continuously fed and removed. Charging with fuel elements is effected intermittently to maintain a fairly high dissolver inventory and thus to achieve a high dissolution rate.

Newby and Rohde[8] have recently described certain of the laboratory studies that resulted in the process. Tests were made in a 1-in.-diameter continuous dissolver with 4*M* to 7*M* HF containing 0.03*M* HNO_3 and 0 to 6 g of boron per liter (added as H_3BO_3 or HBF_4) to dissolve Zircaloy-2 fuel containing 2.2 to 3% uranium. The presence of 4 g of boron per liter created no process problems, and substantially 100% of the boron added was found in the product. Boron was not volatilized significantly, even when the dissolver product was evaporated to dryness. A 5*M* HF dissolving reagent with 4 g of boron per liter was found to be quite satisfactory. A slight tendency was noted for dissolutions involving 4 to 6 g of boron per liter to yield a higher average solids content (0.08 to 0.28 g/liter) than dissolutions in the presence of 2 g of boron per liter (0.02 to 0.14 g of solids per liter). The solids in the high-boron product contained zirconium–fluoride hydrolysis products, whereas those of lower boron content were primarily tin products. Dissolver cleanout (to remove uranium-bearing solids) could be effected with boiling 0.1*M* chromic acid without serious corrosion of the Monel vessel.

Decomposition of Molybdenum Alloys in Alkaline Melts

Molybdenum–uranium alloys are difficult to dissolve completely in nitric acid because of the insolubility of molybdic acid.[9] Baehr has recently proposed that this difficulty can be overcome by treatment of the molybdenum–uranium alloy with an oxidizing alkaline melt ($NaNO_3$, $NaNO_3/NaOH$, or $NaNO_3/Na_2CO_3$) at 500 to 800°C (Refs. 10 and 11). A uranium salt ($Na_2U_2O_7$) is formed which is a crystalline precipitate. This can be filtered readily from the melt, which retains molybdenum in solution. The separation can also be effected by water washing of the cooled melt. The partially decontaminated diuranate can then be dissolved for further processing. The process can also be applied to niobium alloys.

Treatment of Graphite-Matrix Fuels

Studies have been made at both ORNL and the ICPP on burning of graphite-matrix fuels (as used for nuclear rockets and other high-temperature gas-cooled reactors) in a fluidized bed of Al_2O_3 particles in order to provide an ash from which uranium and thorium may be leached to provide a solution for extraction–decontamination.[12] The fluid bed serves to remove the heat of combustion and to improve uniformity of burning. In ORNL work the graphite was crushed to provide $\frac{1}{8}$-in.-diameter particles; whereas, for ICPP studies, pieces of graphite fuel too large to be fluidized have been charged to a fluidized bed of Norton 60 grit Alundum. Recent information[13] on these latter studies has indicated the feasibility of elutriation and separation of the combustion ash from the inert alumina bed to reduce solids-handling requirements and to minimize liquid–solid separation problems.

The tests were conducted in a 4-in.-diameter chamber at fluidization gas velocities of 1 to 1.5 ft/sec. The alumina concentration in the solids carried overhead was less than 0.3%, and approximately 96% of the uranium charged to the burner was elutriated as ash (4% remained in the bed as particles too large to be elutriated). Leaching both elutriated ash and bed resulted in 98 to 99% uranium recovery. The overhead product also contained about 60 wt.% carbon (one-third of that fed to the bed).

The manner of fuel combustion was also indicated by these tests. Inspection of pieces removed from the burner showed that burning occurs primarily on the downward-facing surfaces of pieces near the support grid, whereas pieces from the top of the bed showed little evidence of burning. The surface of the partially burned fuel is granular, and numerous small particles are released as the fuel burns. The particles tend to accumulate in the upper part of the bed because of higher fluidizing-gas velocity in the region of the solid fuel pieces.

Solvent-Extraction Processes

By C. E. Stevenson

Conversion of nitrosylruthenium nitrato complexes to the nitro form by heating with nitrous acid may significantly improve ruthenium decontamination in TBP extraction. Long-chain amine extractants, irradiated to 10^7 r, generally show only minor effects on distribution coefficients for thorium and protactinium extraction, scrubbing, and stripping.

Ruthenium Decontamination in Extraction Processes

Scargill and others at Harwell have extended previous work[14] on improving ruthenium decontamination

in solvent-extraction processes by treatment of feed solutions with nitrous acid.[15] The nitrosylruthenium nitrato complexes have a greater tendency to distribute to the solvent phase than the nitro complexes, and earlier it was shown that, in 3*N* HNO_3–1.25*M* $UO_2(NO_3)_2$ solutions, more than 90% of the RuNO nitrato complexes present could be converted to the nitro form with approximately 0.15*M* HNO_2 at 50 to 60°C for 3 hr. The recent work consisted of miniature extractor tests on process-feed solutions containing added RuNO complexes.

The extraction studies were carried out in a pulsed column (0.7 by 50 cm or 1 by 75 cm) used for the extraction section, plus a small 10-stage mixer–settler for the scrub section. Solvents composed of 20 and 30% TBP were used with organic-to-aqueous flow ratios of 2.1 to 3.4 for the extraction section and 5.1 to 10.8 for the scrub section. The feed contained 1.3*M* $UO_2(NO_3)_2$ in 3*M* or 3.5*M* HNO_3 and 0.002*M* ruthenium as an equilibrium mixture of nitrosylruthenium nitrato complexes. The first portion of each run was carried out with ruthenium in this form, and for the second portion the feed, at 65°C, was sparged with nitrogen oxides for 3 hr, followed by air sparging while cooling. This converted 90% of the nitrato complexes to a mixture of primarily dinitro complexes with a small amount of the mononitro complex. With 20% TBP solvent an overall ruthenium decontamination factor of 90 with RuNO in the nitrato form was improved to 925 with RuNO mostly in the nitro form. With 30% TBP solvent and two different flow rates, the improvement in the ruthenium decontamination factor was from 27 to 60 to 120 to 650. The improvement in ratios agreed closely with values calculated, assuming that complete decontamination from the nitro complex occurs and assuming that no improvement in separation of the remaining nitrato complex occurs. In all cases the major improvement took place at the aqueous feed stage.

It is further noted that, since the limit of conversion of the nitrato complexes is about 90%, the method is only of value for process solutions that do not already contain a large fraction of the ruthenium as nitro complexes. Because of differences in distribution coefficients, less value is expected for application of this technique to processes using Butex as the extractant.

Use of Amine Extractants

The use of long-chain amines as heavy-metal extractants has been of increasing interest because of the relatively high resistance of certain amines to radiation damage and the wide diversity of extraction behavior offered by the selection of suitable amines.[16] Ishihara and Komaki[17] have recently summarized their studies on radiation damage to eight amines in kerosene–lauryl alcohol diluent, as evidenced by alteration in extraction properties.

One primary amine (Primene JMT), four secondary amines (dilaurylamine, laurylcyclohexylamine, and Amberlites LA-1 and LA-2), and three tertiary amines (trioctylamine, benzyldilaurylamine, and cyclohexyldilaurylamine) were examined at 5 vol.% concentration in kerosene containing 5 vol.% lauryl alcohol. The diluted amines were irradiated to 1.5×10^4–1.4×10^8 r with ^{60}Co. Distribution coefficients were measured for equal volumes of extractant and aqueous solutions of (1) 1*M* $Th(NO_3)_4$ or (2) carrier-free ^{233}Pa in 3*N* HNO_3. Scrubbing (3*N* HNO_3) and stripping (0.01*N* HNO_3) tests were also conducted on the irradiated and unirradiated extractants.

For the most part, little changes in distribution coefficients were noted for exposures of $<10^7$ r. The chief exception was for thorium extraction by Amberlite LA-2, which showed a falling-off in distribution coefficient at much less exposure. No marked differences in irradiation behavior were noted for primary, secondary, and tertiary amines except that tertiary amines maintained stripping quality for protactinium at 10^8 r. However, formation of a third phase was noted with the primary and some secondary amines, which suggests less utility for these reagents. In some cases, partition coefficients improved with irradiation.

The extraction behavior of ^{95}Zr and ^{95}Nb in the presence of uranium by a tertiary amine similar to Alamine 336 (in xylene) was recently reported by Minaev and other Soviet workers.[18] A fairly high zirconium–niobium extraction (distribution coefficient above 340) was noted for 0.1*N* to 2*N* H_2SO_4, which is reduced sharply for an organic phase saturated with uranium (distribution coefficient 0.1 from a solution containing 100 mg of zirconium and niobium per liter).

Methods Other Than Extraction for Close-Coupled Processing

By C. E. Stevenson

If means can be devised for the remote refabrication of reactor fuels, by processes and equipment that are relatively insensitive to radiation effects, the decontamination methods used on fuels discharged from reactors need not be restricted by requirements for yielding products that can be handled unshielded by personnel carrying out the refabrication operations. The degree of decontamination from fission products then needed becomes primarily a function of the reactor requirements (i.e., removal of inert materials, nuclear poisons, and other deleterious impurities). This permits the consideration of simplified and presumably more economic processing methods, which might apply in facilities closely re-

lated to a reactor or a small group of reactors. Ferris of Oak Ridge has recently reported[19] a preliminary survey of aqueous processing methods other than solvent extraction which might be utilized in such a close-coupled processing plant. Emphasis was placed on application to thorium–uranium or uranium fuels of the ceramic type, although some of the conclusions presumably apply to metallic fuels and those containing other fissionable and alloying materials.

On the assumption of sol-gel process conversion of the partially decontaminated thorium–uranium recycle fuel to a form suitable for remote refabrication, it was felt that, to be of interest, the process used should be a simple, and preferably single-stage, operation that would yield a gross gamma decontamination factor of at least 100. As solvent-extraction techniques for this purpose were being reviewed in other work, Ferris examined ion exchange, crystallization, and precipitation from aqueous solutions. Since methods for dissolving thoria fuels normally require strong HNO_3, emphasis was also placed on consideration of feed solutions containing $7M$ to $9M$ HNO_3.

Chromatographic separation of uranium and thorium from fission products was first studied using Dowex 1 resin and feed solutions that were $8M$ to $9M$ HNO_3, $0M$ to $0.5M$ HF, and about $0.2M$ $Th(NO_3)_4$–$UO_2(NO_3)_2$ (Th/U = 20). Ten milliliters of feed was sorbed on 11 g of resin, the column was washed with acid of similar concentration, and the uranium and plutonium were eluted with $0.1M$ HNO_3. Good recoveries of the products could be obtained, but the gross gamma decontamination factors were only 20 to 30. Such results were typical of those obtained under a variety of conditions, and significantly greater overall decontamination was not achieved. In addition, it was determined that decontamination was by no means uniform over the fission-product spectrum, the approximate decontamination factors being 100, 3, 400, and 2 for ^{95}Zr, ^{106}Ru, ^{137}Cs, and ^{144}Ce, respectively. The low decontamination achieved for cerium was thought to be particularly significant since it was probably typical of that for other rare earths. Since nuclear poisons are represented among the rare earths, a higher degree of removal would probably be desired. The use of inorganic ion exchangers (such as zirconium phosphate, ammonium molybdophosphate, alumina, and silica gel) was also studied but did not appear attractive because of their instability in strong HNO_3 and the relatively small sorptive capacity of most such materials for fission products at low acidity.

Decontamination achieved by freezing approximately $1M$ solutions of $Th(NO_3)_4$–$UO_2(NO_3)_2$ (Th/U = 15 to 20) in $9M$ or $17M$ HNO_3 was also studied. Temperatures of the order of −30 to −40°C were necessary in order to effect crystallization of a major portion of the thorium, and quantitative recovery was not achieved (only a minor fraction of the uranium crystallized with thorium). Furthermore, thorium decontamination factors were only in the range 3 to 6, and it was therefore felt that a single-step freeze–melt process would not be practical.

The third technique investigated was that of precipitation. Thorium oxalate may be quantitatively precipitated from HNO_3 solution at low to high acidity, but decontamination factors are only of the order of 3 to 5. Uranium(VI) precipitated well only at low acidity and high concentration; U(IV), however, is nearly quantitatively precipitated even in moderately acid solution, but decontamination factors are again quite low. Precipitation of thorium peroxide from $Th(NO_3)_4$ solutions was 94 to 98% complete at $0M$ to $9M$ HNO_3 with decontamination factors of 6 to 7, but, with thorium–uranium solutions, both completeness of precipitation and decontamination factors were lowered. Hydroxides could be precipitated with NaOH, but decontamination was negligible.

General conclusions were that ion exchange, crystallization, and precipitation were not promising as single-step operations for a close-coupled aqueous process plant and that it appeared to be difficult to find an operation that would be superior to solvent extraction for this purpose. It may be commented that, if attention were focused on means for modest removal of a few specific fission products undesirable in continued reactor operation, it is possible that greater success might be achieved in this direction.

Plant and Equipment Design and Operation

By D. M. Paige

A process flow sheet is presented for recovery of thorium and uranium in Savannah River mixer–settler equipment. An equation was developed to correlate a large amount of data from the literature on the flooding behavior of pulse columns.

Mixer–Settler Operation

A dilute Thorex process has been developed at Savannah River applicable to the enriched-uranium chemical separations plant that uses mixer–settler extraction equipment. Kishbaugh reports[20] that, on the basis of tests made in a 14-stage full-sized prototype mixer–settler (type 1A),[21] 3000 lb of thorium per day can be processed through this equipment. The plant mixer–settlers are of two sizes: the 1A size is used generally for extractions, and a slightly larger model (type 1C) is used as an end-fed unit only. Based on the prototype runs, a flow sheet was devised, as shown in Figs. II-3 and II-4, which gives the proposed conditions for the plant (it may be noted that the plant mixer–settlers are 16-stage units instead of 14-stage, as for the prototype).

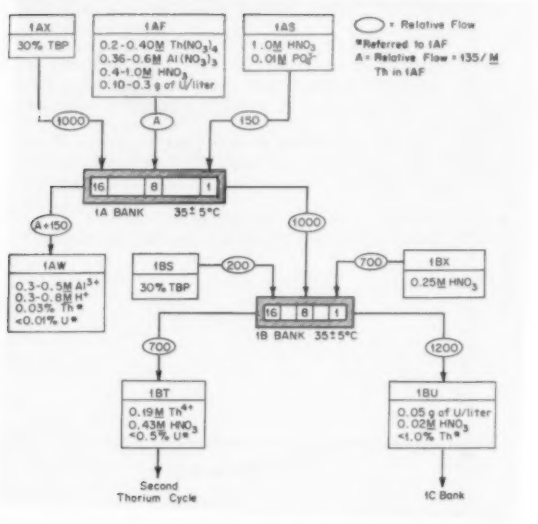

Fig. II-3 First-cycle solvent extraction for thorium processing.[20]

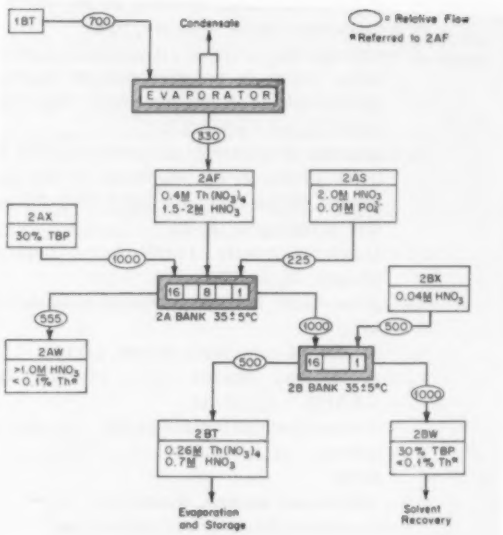

Fig. II-4 Second thorium cycle.[20]

The author presents the following conclusions with reference to the dilute Thorex process indicated in Figs. II-3 and II-4:

1. Extraction capacity will be approximately 3000 lb of thorium per day and is limited by the capacity of the 1B stripping and the second thorium cycle 2A and 2B mixer–settlers.

2. The 1B and 2B banks are hydraulically limited to 3000 lb of thorium per day, both by gross entrainment of the acid strip solution in the solvent stream and by the pressure drop required for solvent flow. Mass transfer is effected at a satisfactory rate with impellers operating at 500 rpm for the 1B unit and approximately 425 rpm for the 2B unit.

3. The 2A bank is hydraulically limited to the 3000-lb rate by the pressure drop required for solvent flow. Mass-transfer rates are satisfactory if the feed acid is maintained at 2.7*M* HNO_3 and if impeller speeds are approximately 425 rpm.

4. Rates for the 1A mixer–settler could reach 4000 lb of thorium per day if the feed concentration were maintained at 0.4*M* maximum and/or if the nitric acid concentration in the 1AS were increased to 2.0*M* with impeller speeds of 450 rpm.

5. The interface levels maintained in the tests were low owing to improperly sized orifices (it was considered that the difficulty of changing the plant mixer–settler orifices would not be worth the benefits, and hence the prototype units were run at less than optimum conditions). The author expected that no problems would be encountered from this source unless the process rates were below 1500 to 2000 lb of thorium per day.

6. The end-stream entrainment was satisfactorily low for all banks at 3000 lb per day.

Pulse-Column Flooding Equation

Over the years since 1935, many experimenters have collected data on pulse columns and have attempted various correlations. A recent ORNL report[22] by Groenier, McAllister, and Ryon presents a very extensive study of many of these data (2200 data points from 20 chemical systems) from numerous sources. The authors, by making use of computer correlations, recommend one of several equations to correlate flooding phenomena in pulsed perforated-plate extraction columns employing two liquid phases. They further state that choosing one equation over others studied was almost impossible but that this one was valid for the entire flooding region. This equation (called No. 122) is:

$$\ln \frac{V_c + V_D}{\Delta_c + \Delta_D} = -3.741 + 0.2568 \ln \frac{\Delta\rho d\epsilon^2}{\rho_c \pi_M^2} - 0.07194 \left(\ln \frac{\Delta\rho d\epsilon^2}{\rho_c \pi_M^2}\right)^2 + 0.006191 \left(\ln \frac{\Delta\rho d\epsilon^2}{\rho_c \pi_M^2}\right)^3 - 1.034 \ln \frac{\mu_c \pi_V}{\epsilon\gamma} + 0.09096 \left(\ln \frac{\mu_c \pi_V}{\epsilon\gamma}\right)^2 + 0.1424 \ln \frac{V_c}{V_D} - 0.1807 \ln \frac{A}{S} + 0.07198 + \left(\ln \frac{\Delta\rho d\epsilon^2}{\rho_c \pi_M^2} \Big/ \ln \frac{\mu_c \pi_V}{\epsilon\gamma}\right)$$

where V_c = continuous-phase velocity, ft/hr
V_D = dispersed-phase velocity, ft/hr
Δ_c = average flow rate of all material past the pulse plates in the direction of the continuous-phase flow, averaged over the entire pulse cycle, ft/hr
Δ_D = average flow rate of all material past the pulse plates in the direction of the dispersed-phase flow, averaged over the entire pulse cycle, ft/hr
$\Delta\rho$ = absolute density difference between phases, lb_m/cu ft
d = pulse-plate hole or perforation diameter, in.
ρ_c = density of continuous phase, g/cm³
π_M = root mean square of π_c and π_D, $\pi_M = \sqrt{0.5(\pi_D^2 + \pi_c^2)}$, ft/hr
μ_c = viscosity of continuous phase, centipoises
π_V = average of π_c and π_D, $\pi_V = 0.5(\pi_D + \pi_c)$, ft/hr
γ = interfacial tension, dynes/cm
ϵ = fractional free area of pulse plates
A = pulse amplitude, in.
S = pulse-plate spacing, in.

The work showed that the equation can be used to predict flow capacities with an average error of 8.56% (predicted value high by this amount) with a standard deviation of 44.70.

A comparison of Eq. 122 with several others is shown in Fig. II-5. Figure II-6 shows how well the calculated and experimental data compare for the equation.

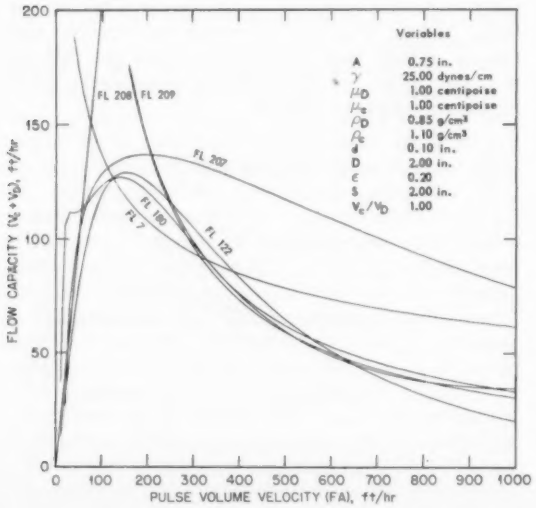

Fig. II-5 Comparison of pulse-column flood Eqs. 7, 122, 180, 207, 208, and 209 (Ref. 22).

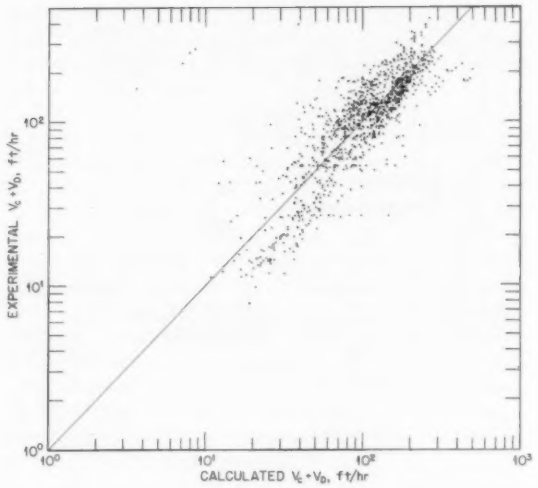

Fig. II-6 Experimental vs. calculated throughput for pulse-column flood Eq. 122 and Group 1 data.[22]

This represents a very brief review of this work, and any extensive use of this equation must involve a careful study of all the material in the report as well as of some of the many original reports from which the data were gathered.

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

By J. J. Barghusen

Various types of processes based on the volatility of uranium and plutonium hexafluorides have been proposed for processing irradiated reactor fuels. Volatility processes are being applied to both highly enriched fuels and ceramic fuels of low enrichment. In these processes, spent reactor fuels are converted to fluorides, and decontamination is carried out by distillation or sorption–desorption methods. A significant feature of several volatility processes under development for both high- and low-enrichment fuels is the application of fluidization techniques to the direct chemical conversion of fuel materials into gaseous compounds. Alternative processes for the recovery of uranium from fuel materials are the Nitrofluor and the fused-salt volatility processes.

Nitrofluor Process

The Nitrofluor process for treating spent reactor fuels is based on dissolution of the fuel in anhydrous hydrogen fluoride solutions containing complexing agents in the form of N_2O_4, N_2O_3, or NOF. These solutions are capable of dissolving a wide variety of fuels owing to the reactivity of the nitrosyl ion (NO^+) in the solvent. After the fuel is dissolved, the liquid phase is evaporated and the solid residue is fluorinated to separate uranium and plutonium from fission products. Recent work at Brookhaven National Laboratory (BNL)[1] has been concerned with engineering-scale demonstrations of the dissolution of uranium–zirconium alloy fuel in the 95°C azeotrope solvent (NOF · 3.1 HF ·<0.1 N_2O_3). The dissolution tests were performed in a 6-in.-diameter dissolver that was cooled by circulating anhydrous HF through an internal helical coil. The multiplate assemblies of uranium–zirconium alloy iuel were suspended within the dissolver by a Monel wire. In a test involving the dissolution of a 7.8-kg assembly in 21 gal of solvent, the temperature of the solvent increased from 25 to 120°C within 5 min. The average dissolution rate within this period was 227 g of zirconium per minute. The NO gas evolved was vented continuously at 70 psig. The reaction rate subsequently decreased, and throughout the remainder of the test only intermittent venting and cooling of the system was required. Periodic additions of solvent were made to maintain a constant liquid level in the dissolver. Nitrogen sparging of the system increased the dissolution rate to 409 g of zirconium per minute. Complete dissolution of the multiplate assembly was accomplished in 2¼ hr.

Tests were also performed on the dissolution of sintered UO_2 clad in stainless steel and on a multiplate assembly of uranium–aluminum alloy. After 4 hr of dissolution at 110 to 116°C, all the UO_2 and stainless-steel cladding had dissolved; only small fragments, such as end caps, remained undissolved. The dissolution of a 5.2-kg uranium–aluminum alloy assembly was carried out at 116 to 127°C. After 12 hr only 186 g of aluminum metal remained in the dissolver.

The separation of uranium from dissolved fuels was studied on a laboratory scale using BrF_3 to volatilize UF_6 from the complex salt mixture that remained in the dissolver after evaporation of the solvent. In a test using the complex salt derived from the dissolution of zirconium–uranium alloy fuel, a series of five BrF_3 treatments at 135 to 150°C removed 99.4% of the uranium in the salt. Similar experiments with salt derived from uranium–aluminum alloy fuel also showed high uranium removal by contact of the salt with BrF_3 at 150°C. Extensive drying of the uranium–aluminum salt decreased uranium recovery during fluorination. Other techniques for recovering uranium that are being studied involve the volatilization of $NOUF_6$ by contacting the dissolver solids with NOF gas at 400°C and the volatilization of UF_6 from the dissolver solution by the action of fluorine. The latter method is based on the reaction of hydrogen fluoride with dissolved $NOUF_6$ to produce UF_5, which is readily converted to UF_6 by the addition of fluorine to the system.

Volatility Processes for High-Enriched Fuels

A fluid-bed volatility process for the recovery of uranium from highly enriched uranium-alloy fuels is being developed at Argonne National Laboratory (ANL).[2,3] The research effort at ANL is divided into two phases: (1) the demonstration of the process in a pilot-scale facility designed to handle up to 30-kg

charges of uranium–zirconium alloy and 14-kg charges of uranium–aluminum alloy, and (2) evaluation of the process in a bench-scale facility using irradiated alloy fuel elements. Reference 2 describes the results of the final six runs in the pilot-plant facility; these runs complete the development program at ANL on unirradiated alloy fuels. (A description of the pilot-scale facility and the progress of engineering development work in the facility have been presented in previous issues of *Reactor Fuel Processing*.[4–6])

The experimental program with irradiated fuels is primarily directed toward obtaining information regarding (1) the distribution of fission products during the various process steps, (2) decontamination factors that may be realized, and (3) the effects, if any, of irradiation and the presence of fission products on uranium recovery.

Two basic steps are involved in the processing of uranium–zirconium and uranium–aluminum alloy fuels. In the first step the fuel is reacted with hydrogen chloride gas to form volatile chlorides of zirconium or aluminum which separate from nonvolatile uranium trichloride. In the next step uranium is removed from the reactor as UF_6 by fluorination with fluorine and is collected on sodium fluoride pellets. Further purification of the collected UF_6 can be achieved by desorption from NaF and collection of the UF_6 in cold traps.

In the bench-scale facility, the volatile $ZrCl_4$ (or $AlCl_3$) generated in the first step is collected as a solid in a condenser. The noncondensables pass through a glass-wool filter and then into a scrubber wherein HCl is removed from the process gas stream. The UF_6 produced in the second step passes through a packed-bed filter, then through a NaF trap at 400°C to remove fission products, and is sorbed on NaF pellets at 100 to 150°C. Residual UF_6 in the gas stream is collected in a backup NaF trap maintained at 25°C. Excess fluorine in the gas stream is reacted with activated alumina. Remaining gases are discharged to the building exhaust system.

Demonstration tests were performed with both uranium–zirconium and uranium–aluminum alloy fuels.[3] Hydrochlorination was carried out at 400°C with 40 vol.% HCl in nitrogen for uranium–zirconium alloy and at 250°C with 20 vol.% HCl for uranium–aluminum alloy. The fluorination step employed a procedure whereby, during the initial period, the temperature of the fluidized- and packed-bed filter was slowly increased from 250 to 500°C and the fluorine concentration was increased from 5 to 75 vol.%; the final period was carried out at 500°C with 75 vol.% fluorine at low flow rates such that the reactor bed was maintained under static conditions. The results of two tests with 5-year-cooled uranium–zirconium alloy fuel are presented in Fig. III-1. In these tests the alloy charges weighed 270 g and contained 4.9 g of uranium and 3.3 g of fission products. The distribution of activities following the processing of irradiated, 3-month-cooled uranium–aluminum alloy appears in Fig. III-2 and Table III-1. On the basis of tests performed with irradiated and unirradiated fuel materials, the presence of fission products from irradiated fuel had no marked effect on uranium recovery or loss. During the hydrochlorination step the fission products cerium, cesium, strontium, and ruthenium were essentially nonvolatile under the conditions employed. The elements that exhibited slight volatility (<10%) were antimony, tellurium, and technetium. The predominantly volatile species (>50%) were zirconium, niobium, and krypton. Iodine volatilized completely during the hydrochlorination step. A caustic scrubber was successful in effecting the removal of iodine from the process off-gas stream.

The distribution of the fission-product elements following the fluorination step showed that cerium, cesium, and strontium are essentially nonvolatile and are retained on the reactor and filter beds. Ruthenium was also nonvolatile; less than 1% volatilized and collected in the fission-product trap. The fission products that were found to be predominantly volatile (>50%) were molybdenum, technetium, and tellurium. The complete removal of tellurium from the process off-gas during the fluorination step was effected by the use of an activated-alumina trap.

Uranium decontamination factors, in general, increased by one or two orders of magnitude by desorbing the UF_6 product from the sodium fluoride and collecting the UF_6 in cold traps. This technique did not affect the removal of technetium from the UF_6, however.

Volatility Processes for Uranium Carbide and Graphite-Base Fuels

Engineering-scale studies on methods for processing graphite–uranium carbide fuels are being conducted at BNL[1] in fluid-bed equipment. These studies are applicable to the Rover Nuclear Rocket fuel, the High-Temperature Gas-Cooled Reactor (HTGR) fuel, and other fuels containing uranium carbide in a graphite matrix. The processing scheme basically consists in oxidation of the graphite and uranium carbide by oxygen to convert the graphite to CO and CO_2 and to convert uranium (and thorium in the case of HTGR fuel) and other materials in the fuel to their respective oxides. The nonvolatile oxide ash is then treated with fluorine to recover uranium as UF_6.

Descriptions of the BNL facility and results of tests with Rover fuel and HTGR fuel were presented in previous issues of *Reactor Fuel Processing*.[7,8] The data on the processing of HTGR fuel given in Ref. 1 were previously reviewed.[8]

Scott[9] has prepared a mathematical analysis of the oxidation of graphite–uranium carbide fuel in fixed or moving beds and has applied the results of this analysis to the prediction of the behavior of large-scale oxidation reactors. The major problems to be

expected in this reaction system are: excessive CO content of the gas; excessive fuel temperature, which may result in ash melting or sintering; and excessive wall heat flux. Zone oxidation or depletion of the oxygen content of the gas stream in a relatively small section of the fixed bed is also an important factor. Changes in gas flow rate, oxygen composition of the inlet gas, oxidation-ash buildup, fuel particle size, and reactor type have the following general effects on system behavior:

Gas Flow Rate. An increase in gas flow rate results in an increase in maximum system temperature, maximum CO content, maximum wall heat flux, and length of oxidation zone up to the point that increase in convective heat transfer results in a decrease in the system temperature, after which the maximum CO content and maximum wall heat flux decrease with increasing gas flow rate.

Oxygen Composition of Inlet Gas. A decrease in the oxygen content of the inlet gas (by dilution with an inert gas) decreases the maximum system temperature, CO content, and wall heat flux, but increases the length of the oxidation zone.

Oxidation-Ash Buildup. The presence of oxidation ash has the same effect on operating results as a decrease in the oxygen content of the inlet gas.

Fuel Particle Size. Reducing the fuel particle size gives a higher reaction rate and results in operational problems of high temperatures and CO concentration. Fairly large particles should be used.

Reactor Type. Reducing the tubular reactor size results in a reduction in temperature and CO content for the same mass flow rate; thus several small reactors are individually easier to control than one big one. An annular reactor gives lower temperature and CO content than a tubular reactor of the same

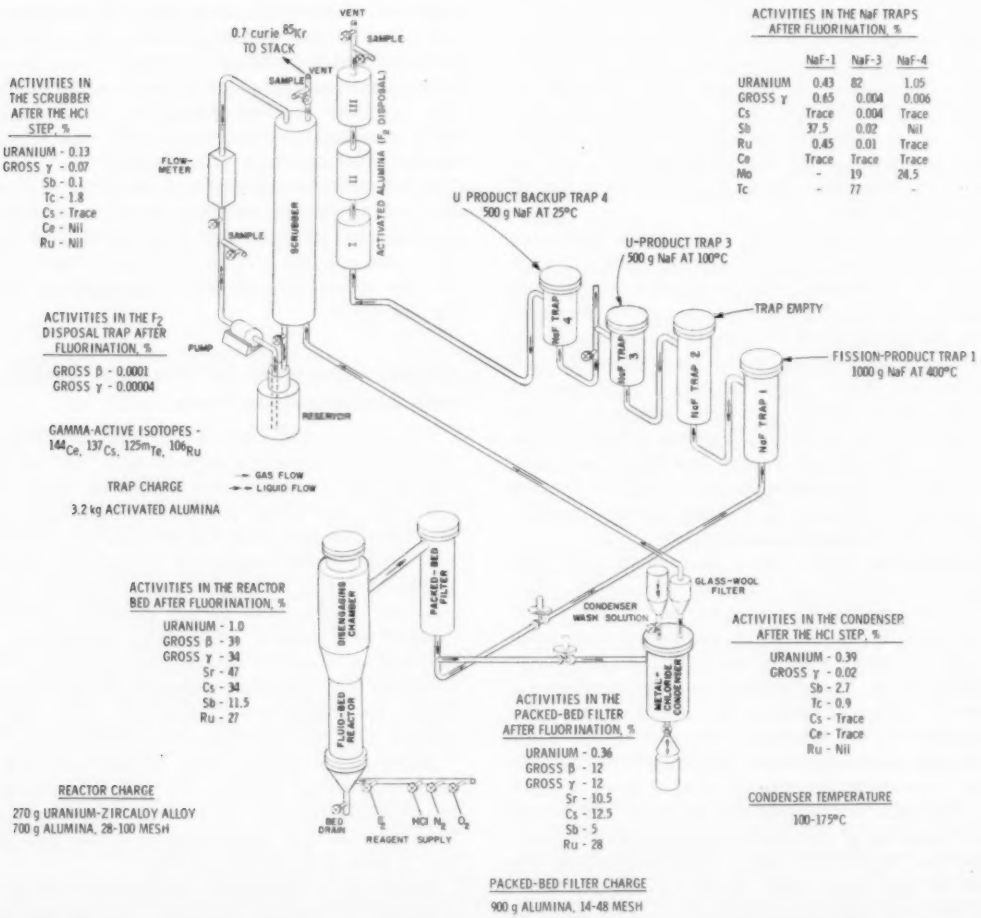


Fig. III-1 The distribution of uranium and fission products following fluid-bed volatility processing of irradiated 5-year-cooled uranium–Zircaloy alloy.[3] (The values are the averages for two runs and are in percent of the total activity charged to the reactor.)

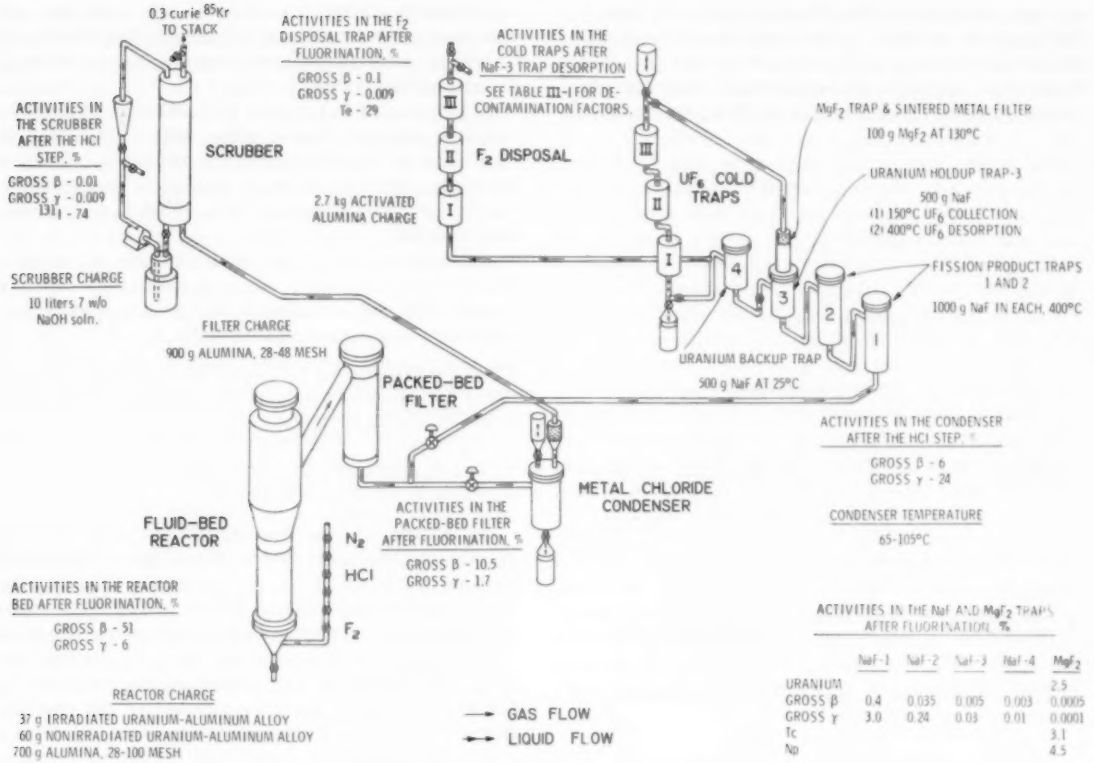

0.3 curie 85Kr TO STACK
ACTIVITIES IN THE F2 DISPOSAL TRAP AFTER FLUORINATION, %
GROSS β - 0.1
GROSS γ - 0.009
Te - 29
ACTIVITIES IN THE COLD TRAPS AFTER NaF-3 TRAP DESORPTION
SEE TABLE III-I FOR DECONTAMINATION FACTORS.
MgF2 TRAP & SINTERED METAL FILTER
100 g MgF2 AT 130°C
ACTIVITIES IN THE SCRUBBER AFTER THE HCl STEP, %
GROSS β - 0.01
GROSS γ - 0.009
131I - 74
SCRUBBER
F2 DISPOSAL
UF6 COLD TRAPS
URANIUM HOLDUP TRAP-3
500 g NaF
(1) 150°C UF6 COLLECTION
(2) 400°C UF6 DESORPTION
2.7 kg ACTIVATED ALUMINA CHARGE
FISSION PRODUCT TRAPS 1 AND 2
1000 g NaF IN EACH, 400°C
SCRUBBER CHARGE
10 liters 7 w/o NaOH soln.
FILTER CHARGE
900 g ALUMINA, 28-48 MESH
URANIUM BACKUP TRAP
500 g NaF AT 25°C
PACKED-BED FILTER
ACTIVITIES IN THE CONDENSER AFTER THE HCl STEP, %
GROSS β - 6
GROSS γ - 24
METAL CHLORIDE CONDENSER
CONDENSER TEMPERATURE
65-105°C
FLUID-BED REACTOR
ACTIVITIES IN THE PACKED-BED FILTER AFTER FLUORINATION, %
GROSS β - 10.5
GROSS γ - 1.7
N2
HCl
F2
ACTIVITIES IN THE REACTOR BED AFTER FLUORINATION, %
GROSS β - 51
GROSS γ - 6
REACTOR CHARGE
37 g IRRADIATED URANIUM-ALUMINUM ALLOY
60 g NONIRRADIATED URANIUM-ALUMINUM ALLOY
700 g ALUMINA, 28-100 MESH
GAS FLOW
LIQUID FLOW
ACTIVITIES IN THE NaF AND MgF2 TRAPS AFTER FLUORINATION, %
NaF-1 NaF-2 NaF-3 NaF-4 MgF2
URANIUM 2.5
GROSS β 0.4 0.035 0.005 0.003 0.0005
GROSS γ 3.0 0.24 0.03 0.01 0.0001
Tc 3.1
Nb 4.5

Fig. III-2 The distribution of activities following fluid-bed volatility processing of irradiated 3-month-cooled uranium–aluminum alloy.[3] (Values given are the averages for two runs and are in percent of the total activity charged to the reactor.)

cross-sectional area because of its additional heat-transfer area.

Moving Bed. A moving-bed annular reactor operating at steady state results in a high production rate, with limited operational problems. This, of course, discounts mechanical problems that may be associated with such a reactor.

Several methods for treating sintered uranium carbide fuel material in preparation for uranium recovery by volatility techniques are being studied at Centre d'Étude de l'Énergie Nucléaire (CEN) at Mol, Belgium.[10] These methods involve the conversion of the carbide fuel to powdered uranium oxide or uranium fluoride that is readily fluorinated to UF_6. Recent work has concerned evaluating gaseous mixtures of HF and oxygen to convert sintered UC to a powdered mixture of UF_4 and UO_2F_2. The reaction temperature markedly affects the extent of carbon removal; at temperatures below 200°C nearly all the carbon remains within the system, whereas at 500°C and above carbon removal is essentially complete. At 500°C the composition of the solid product varies with changes in the concentration of HF in oxygen. As the concentration of HF is increased, the concentration of UF_4 in the product increases, with a corresponding decrease in the concentrations of UO_2F_2 and uranium oxides. Temperatures of 500°C and oxygen concentrations of 20 to 40 vol.% in HF are the most satisfactory in that these conditions result in high carbon removal and the formation of a powdered solid containing high concentrations of UF_4.

Table III-1 DECONTAMINATION FACTOR FOR IRRADIATED URANIUM–ALUMINUM ALLOY FUEL[3]

Activity	Decontamination factor	Activity	Decontamination factor
Gross gamma	2×10^7	Antimony	5×10^5
Gross beta	1×10^8	Zirconium	7×10^7
Cerium	1×10^7	Niobium	4×10^7
Strontium	1×10^7	Technetium	1
Cesium	4×10^6	Neptunium	3
Ruthenium	6×10^5	Plutonium	4×10^6

Aqueous-Volatility Process

A U. S. patent[11] on a process for the recovery of uranium and plutonium from irradiated fuels based on ion-exchange and fluoride-volatility techniques

has been assigned to the General Electric Company. The process utilizes a head-end step wherein the fuel is dissolved in nitric acid (~7*N*) and then contacted with a bed of anion-exchange resin for plutonium recovery (see Fig. III-3). The plutonium and

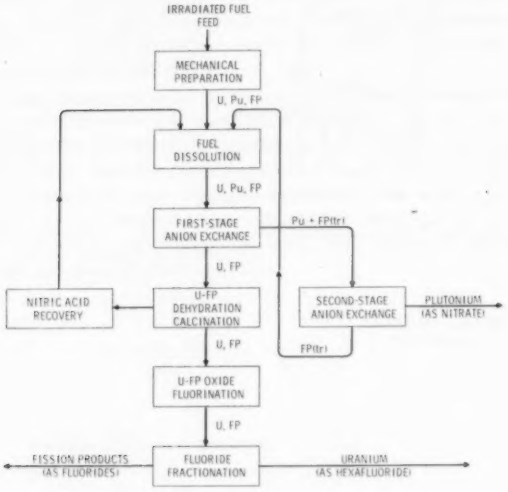


Fig. III-3 Reprocessing irradiated low-enrichment fuel by aqueous-volatility techniques.[11]

a small portion of the fission products are retained within the resin, whereas the uranium and substantially all the fission products appear in the effluent stream. The plutonium is then eluted from the resin, and final decontamination is performed by a second anion-exchange step. The uranium-bearing effluent stream is passed to an evaporator to form a concentrated solution of about 60 to 100% uranyl nitrate hexahydrate. The concentrated solution is then calcined at 300°C to form an anhydrous mixture of uranium and fission-product oxides. The calcined solids are contacted with hydrogen fluoride at 250 to 350°C and then with fluorine at temperatures between 300 and 600°C. The products from the fluorination step consist primarily of uranium hexafluoride and volatile fission-product fluorides. Initial separation of the UF_6 from the volatile fission-product fluorides is achieved by partial condensation of the less volatile fluoride species. Final purification of UF_6 is achieved by fractional distillation.

Volatility Processes for Low-Enriched Fuels: Processing of UO_2 Fuels

In the fluoride-volatility processing of UO_2 fuels, the fuel is first declad and then pulverized to produce a powdered material highly reactive towards fluorination. Processes based on the use of three different fluorinating agents are being developed:

1. Reaction with fluorine wherein uranium and plutonium are both converted to volatile hexafluorides; plutonium is then separated from uranium by thermal decomposition of PuF_6 to PuF_4.
2. Reaction with bromine pentafluoride to produce volatile uranium hexafluoride while plutonium is converted to nonvolatile PuF_4, thereby achieving a separation of uranium from plutonium; plutonium is recovered in a subsequent step as PuF_6 by reaction with fluorine.
3. Reaction with chlorine trifluoride to achieve separation of uranium from plutonium by forming volatile UF_6 and nonvolatile PuF_4; plutonium is then recovered by reaction with fluorine.

Final purification of UF_6 may be achieved by fractional distillation or by selective sorption–desorption on a bed of NaF pellets.

DECLADDING OF STAINLESS-STEEL- AND ZIRCALOY-CLAD UO_2 FUEL

Decladding of stainless-steel-clad UO_2 fuel is readily accomplished by reaction of the cladding with gaseous mixtures of HF and oxygen in a fluid bed of inert alumina particles at 550 to 600°C. This reaction produces a rapid disintegration of the cladding by fluoride-promoted oxidation and exposes the uranium and plutonium for subsequent fluorination. As the sintered oxide becomes exposed to the reacting gases, the fuel reacts with the gases to form a powdered mixture of oxides and fluorides. Workers at BNL[1] have demonstrated the decladding of stainless-steel-clad UO_2 in a 4-in.-diameter fluid-bed reactor using multirod assemblies, 15 and 30 in. long. The assemblies were reacted with 40 vol.% HF–60 vol.% oxygen at 600°C using a superficial gas velocity of 0.75 ft/sec. As the UO_2 pellets became exposed, the HF concentration was decreased to 25 vol.% to promote pulverization of UO_2 to U_3O_8 and to minimize the formation of UO_2F_2. The decladding and pulverization of UO_2 pellets were complete within 4.5 hr. To determine the effect of stainless-steel decladding products on the recovery of uranium as UF_6 by reaction with fluorine, the workers contacted the bed from the decladding step with 25 vol.% fluorine in nitrogen at 450°C for 2.5 hr. The fluorination reaction was completed by a 1-hr exposure to 50 vol.% fluorine at 525°C. In all tests the reactions proceeded without any indications of temperature excursions or caking of the bed.

Workers at CEN[10] have observed a significant difference in the susceptibility of various types of stainless steel toward mixtures of HF and oxygen. At 550°C, with the use of an equimolar mixture of HF and oxygen in the absence of alumina, types 304, 316, and 348 exhibited penetration rates of 538, 380, and 20 μ/hr, respectively. Comparison of results of experiments performed in a boat reactor with those performed in a fluid bed showed that the rate of reaction of stainless steel with HF–oxygen mixtures

was uniformly lower in fluid beds. An increase in temperature of the fluid bed of about 25 °C was required to achieve reaction rates identical to those achieved in the boat reactor. Apparently the action of the fluid bed avoids the occurrence of local high-temperature regions on the samples and thus results in a slight reduction in the overall reaction rate.

The use of HF–oxygen mixtures is also being considered for decladding of Zircaloy-clad fuel.[1,10] The effects of temperature and concentration of HF on the rates of reaction were discussed in a previous issue of *Reactor Fuel Processing*.[12]

Development work is also being carried out on the use of HCl for the decladding of Zircaloy-clad UO_2 fuel.[3] Hydrogen chloride reacts with the cladding to form volatile $ZrCl_4$, which is removed from the reactor. A demonstration test was performed at ANL[3] in which a fuel bundle consisting of 25 Zircaloy-2 tubes, 28 in. long, and filled with 15.8 kg of UO_2 pellets was declad in a 6-in.-diameter fluid-bed reactor. The tubes were mounted in a square array with 0.14-in. spacing between tubes. The bundle was immersed in a fluid bed of refractory alumina particles and contacted with 40 to 85 vol.% HCl at a bed temperature of 395 °C. The off-gas from the fluid-bed reactor was filtered through an 11.5-in.-deep packed bed (14.7 kg) of 14- to 48-mesh alumina. Progress of the decladding reaction was continuously monitored by hydrogen analyses of the off-gas stream and by gamma-ray photography of the tube bundle (see Fig. III-4). The bundle reacted gradually from the bottom to the top, and, as the reaction progressed, the fuel bundle gradually immersed deeper into the fluid bed. The UO_2 pellets, which are unaffected by HCl, collected to form a packed bed at the bottom of the reactor. Both the off-gas analyses and gamma-ray photography indicated that the decladding step was complete in 4.5 hr. The average reaction rate was 0.9 kg of Zircaloy-2 per hour, and the HCl utilization efficiency averaged 17%. The uranium loss due to transport with the off-gas stream exiting from the packed-bed filter was less than 0.004% of the uranium charged in the fuel bundle.

A study was made to determine the feasibility of decladding long fuel bundles in a shallow fluidized bed. A fuel bundle, 70 in. long, consisting of two solid Zircaloy-2 rods and four Zircaloy-2 tubes packed with UO_2 pellets was contacted with 48 to 64 vol.% HCl at 400 °C in a 14-in.-deep fluidized bed.[13] Decladding was completed in 4.5 hr.

After 2 hr of reaction, one of the Zircaloy rods was removed from the reactor and the diameter measured along the entire length. The penetration rates, calculated from dimensional changes, averaged 17 mils/hr for the portion of the rod immersed in the fluid bed and 34 mils/hr at the interface between

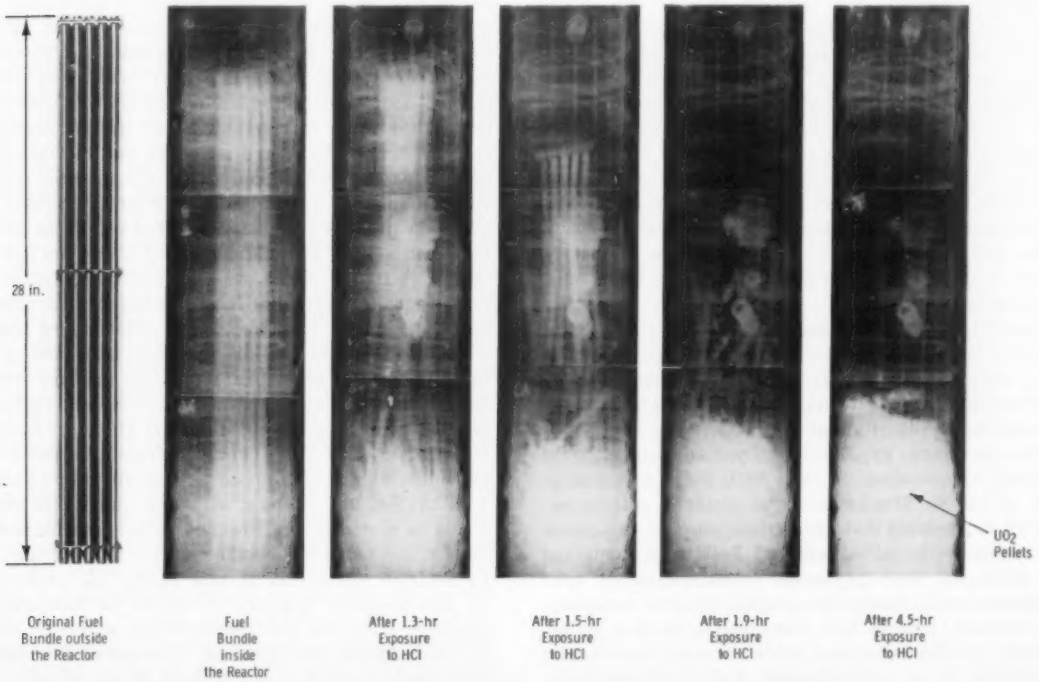

28 in.
UO2 Pellets
Original Fuel Bundle outside the Reactor
Fuel Bundle inside the Reactor
After 1.3-hr Exposure to HCl
After 1.5-hr Exposure to HCl
After 1.9-hr Exposure to HCl
After 4.5-hr Exposure to HCl

Fig. III-4 Decladding of Zircaloy-2-clad UO_2 fuel bundle in a fluid-bed reactor.[3]

the fluid bed and the gas phase. The highest rate of penetration (to 75 mils/hr) occurred at the portion of the rod located above the fluid bed in a zone where the diameter of the fluid-bed reactor increases from 6 in. to 12.5 in. The portion of the rod above the fluid bed was covered with a friable scale of varying thickness (2 to 10 mils). No scale was observed on the portion of the rod that had been immersed within the bed; evidently the scale was removed from the rod by the action of the bed.

A temperature profile was obtained for the second Zircaloy rod from 12 thermocouples spot-welded to the rod at 6-in. intervals. In the fluid-bed zone, the temperature of the rod was identical to that of the bed (400°C), thereby indicating that the heat transfer from the surface of the rod to the bed was good. In the gas phase above the bed, the temperature of the rod was much higher, up to 640°C, although the temperatures of the surrounding gas and the reactor wall were 400°C, thus indicating that the heat transfer from the rod to the surroundings was poor. The highest temperature was observed at a position equivalent to the position where the highest penetration was measured on the companion rod.

On the basis of these data on penetration rates and temperature measurements, it probably is possible to declad long fuel bundles in shallow fluid beds.

PRETREATMENT OF UO_2 FOR VOLATILITY PROCESSING

Several methods for treating UO_2 or UO_2-PuO_2 fuel materials in preparation for uranium and plutonium recovery by fluoride-volatility techniques are being studied at CEN.[10,14,15] These methods involve the conversion of sintered UO_2 to powdered U_3O_8 (or UO_2-PuO_2 to powdered $U_3O_8-PuO_2$) by reaction with oxygen and the reaction of the powdered oxides with hydrogen fluoride to form a powdered mixture of fluorides and oxyfluorides. Reference 14 summarizes development work at CEN on these conversion reactions and presents the results of studies on the effects of fission products and plutonium on the rate of the reactions.

Results previously reported in *Reactor Fuel Processing*[16] have shown that the extent of conversion of UO_2 and U_3O_8 was unaffected by the presence of up to 10 mole % PuO_2 but was greatly limited with oxides containing 20 to 40 mole % PuO_2. Brett and Fox[17] have examined by X-ray diffraction the products formed by oxidation of UO_2-PuO_2 solid solutions in air at 750°C. The oxidation of sintered pellets resulted in products that were either one- or two-phase according to the initial material. Pellets that contained at least 40 at.% plutonium remained intact upon oxidation and retained the original fluorite structure. In contrast, pellets that contained up to 10 at.% plutonium disintegrated upon oxidation and produced solid solutions of an orthorhombic U_3O_8 type structure. Oxidation of pelleted materials of intermediate compositions produced varying binary mixtures of cubic and orthorhombic phases. The oxidation products of $(U,Pu)O_2$ powders differed from the products obtained from pellets of similar composition. Single orthorhombic phases were obtained from powders that contained 1 and 2 at.% plutonium, whereas two-phase (cubic and orthorhombic) products were found in powders of compositions between 4.9 and 40 at.% plutonium.

In the decladding of stainless-steel- or Zircaloy-clad UO_2 by reaction of the cladding with HF–oxygen mixtures, the UO_2 reacts with the gas mixture to form a powder containing U_3O_8 and UO_2F_2. Laboratory-scale experiments were performed at BNL[1] to determine the processing conditions that promote the formation of U_3O_8 rather than UO_2F_2. With a gaseous mixture of 20 vol.% HF–80 vol.% oxygen at 600°C, a finely divided product that contained primarily U_3O_8 was obtained. At higher HF concentrations both the concentration of UO_2F_2 in the product and the average particle size of the product increased.

REACTION OF UO_2-PuO_2 FUEL WITH FLUORINE

An engineering-scale high-alpha facility has been constructed at ANL[2,3] to study steps in the processing of UO_2-PuO_2 fuel materials by fluoride-volatility processes. Descriptions of the facility and process equipment have appeared in previous issues of *Reactor Fuel Processing*.[18,19] The primary objectives of experiments performed in the engineering-scale facility are (1) to investigate the behavior of PuF_6 in process equipment and determine the nature of any difficulties in handling PuF_6 and (2) to determine the feasibility of fluoride-volatility flow sheets. In the flow sheet under current investigation, the fluorination of UO_2-PuO_2 sintered pellets is carried out by the two-zone oxidation–fluorination method. The pellets in the form of right cylinders (0.5 in. in diameter by 0.5 in. long) are added to the fluorinator to form a packed bed supported on a 3-in.-deep bed of ¼-in.-diameter nickel balls. Sintered alumina is added to provide a fluidized-packed bed in the pellet zone and a 2-ft-deep fluidized bed above the pellets (see Fig. III-5). In the two-zone oxidation–fluorination process, oxygen diluted with nitrogen is introduced into the bottom of the fluorinator. The oxygen reacts with the sintered pellets to form U_3O_8 and PuO_2 fines (generally less than 200 mesh) that are transported into the fluidized-bed zone where they are reacted with a separate fluorine stream, forming volatile UF_6 and PuF_6. Four fluorine inlet ports are provided; as the pellet bed is consumed by reaction with oxygen, the position at which fluorine is introduced is successively lowered. After approximately 95% of the oxide has been converted to hexafluorides by fluorine introduced at side ports, the production of hexafluorides appears to cease as indicated by readings from the continuous-weigh scales on which the cold traps are mounted. Thereafter fluorine is introduced instead at the bottom of the reactor, and the reaction is continued for a period of 1 or more hours, depending on the extent of production of addi-

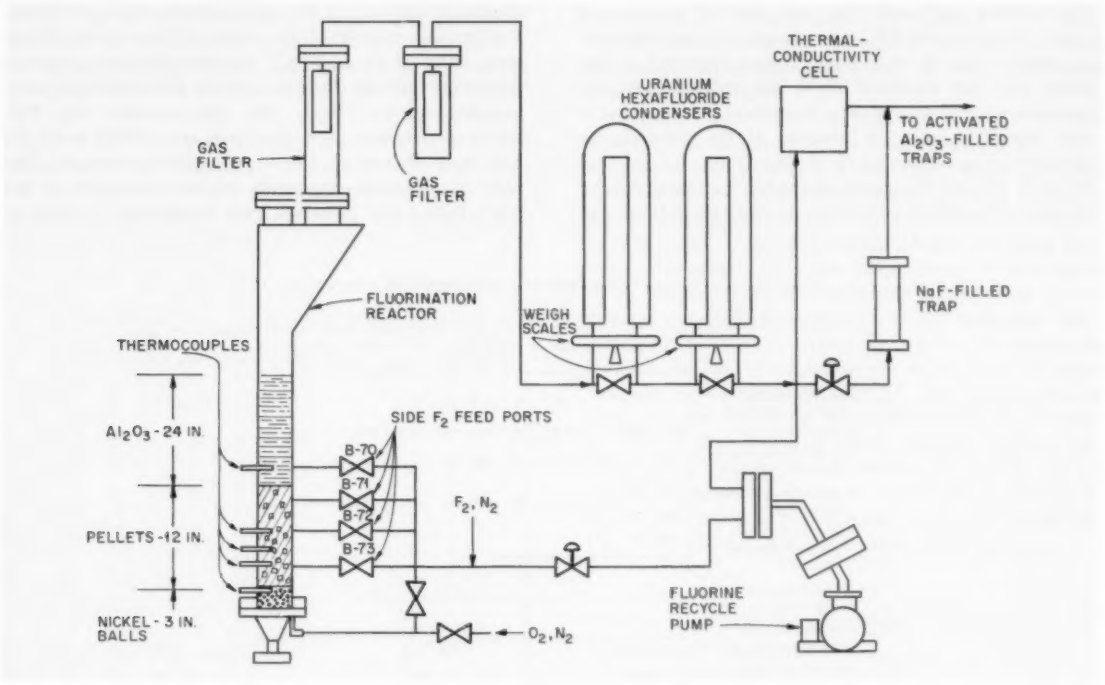


Fig. III-5 Fluorination-process equipment.[3]

tional hexafluoride. During this period, recycle of the fluorine off-gas is often employed as an economy measure. This single-zone reaction period is followed by a fluorine recycle (cleanup) period in which the remainder of the uranium and plutonium are recovered from the reactor. The cleanup period is characterized by the use of higher fluorine concentrations (90 vol.% fluorine) and higher temperatures (550°C) than those in either the two-zone reaction period or the single-zone fluorination period.

Operating conditions for the initial run in the facility with UO_2-PuO_2 fuel are presented in Table III-2. The charge for this run consisted of 1.8 kg of UO_2 pellets and 7.0 kg of 0.5 wt.% PuO_2-UO_2 pellets. Approximately 6.5 kg of nominal 48- to 100-mesh alumina particles were used as the bed material. The final uranium and plutonium concentrations in the alumina bed from this run were each 0.02 wt.%. For a single use of the alumina bed, these values correspond to removals of about 99.9% and 95% of the uranium and plutonium in the charge. (In practice it is expected that the same alumina bed would be used for the fluorination of several batches of fuel.) When the alumina bed was removed from the reactor after the run, it was observed that a finely divided solid material containing plutonium had been held up on reactor surfaces above the bed. This material evidently had been elutriated from the bed during the run and had not been completely fluorinated. Several techniques are being investigated to reduce this holdup of fines and to return the fines to the bed where they will be reacted during fluorination.

In the development of the two-zone oxidation–fluorination process at ANL, considerable attention was directed toward a study of the gas-mixing, solids-mixing, and heat-transfer behavior in fluidized–packed beds. Results of these studies were recently published.[20–25]

FLUORINATION WITH CHLORINE TRIFLUORIDE

Of major concern in the development of fluoride-volatility processes for low-enrichment UO_2 fuel is establishing methods for the separation of uranium from plutonium and for the recovery of plutonium. A method under development at CEN[10,14,15] for effecting the separation of uranium from plutonium involves the selective fluorination of uranium from the mixed fluorides ($UF_4-UO_2F_2-PuF_4$) with chlorine trifluoride. Plutonium is recovered as PuF_6 in a subsequent step by fluorination of the solid PuF_4 with fluorine. A series of laboratory-scale investigations was carried out[10] to determine the effects of the presence of plutonium and synthetic fission products on the reaction cycle

$$(U,Pu)O_2 \xrightarrow{O_2} U_3O_8 + PuO_2 \xrightarrow{HF}$$

$$UF_4 + UO_2F_2 + PuF_4 \xrightarrow{ClF_3} UF_6 + PuF_4 \xrightarrow{F_2} PuF_6$$

The results indicated that the rate of reaction of $U_3O_8 + PuO_2$ toward HF is decreased with the presence of greater than 2 wt.% PuO_2. It was observed in this study that the products from the hydrofluorination reaction exhibit a tendency to sinter; it is suggested that sintering can be avoided if the reaction is initiated at a temperature of 350°C for 0.5 hr with 30 vol.% HF and then continued at 400°C. The presence of up to 20 mole % plutonium in the mixed fluorides does not markedly affect the rate of uranium fluorination by ClF_3 at 105°C; however, the effect does become marked at higher plutonium concentrations (38 mole %).

In an effort to simplify the process scheme, a series of tests was performed[10,15] to evaluate the direct fluorination of sintered UO_2 pellets with ClF_3. The tests were carried out in a 3.4-cm-diameter reactor using charges containing 500 to 1000 g of sintered UO_2. At 100°C it was observed that the presence of fission-product oxides in the UO_2 pellets and also the presence of an alumina fluid bed resulted in a decrease in the rate of reaction between UO_2 and ClF_3. This effect became more pronounced at 300°C. The rate of reaction at 100°C varied inversely with the density of the UO_2 pellets and directly with the ratio of pellet surface to pellet weight. The effect of pellet density on reaction rate was virtually absent at 300°C. The addition of fluorine to the ClF_3 gas stream (up to 40% of the ClF_3 flow) produced a marked increase in the rate of conversion of sintered UO_2 to UF_6 at 300°C. Evidently the effect of fluorine is to reconstitute the ClF_3 by fluorinating the reaction products.

In connection with this work, a study is under way to measure the kinetics of the reactions between powdered UO_2 and ClF_3 and between U_3O_8 and ClF_3. Preliminary results of the study of the reaction of UO_2 with ClF_3 at 50 to 300°C indicate that the reaction proceeds through the formation of intermediate compounds, namely, UO_2F_2, UF_4, and perhaps UF_5. The reaction between U_3O_8 (particle size 500 μ) and ClF_3 has been studied at 150°C in a flowing system. The rate of reaction was only slightly sensitive to the ClF_3 flow rate. Reaction rate constants of 0.078 to 0.091 min^{-1} were calculated using a diminishing-sphere model.

Table III-2 OPERATING CONDITIONS FOR PROCESSING UO_2-PuO_2 FUEL[3]

Run time, hr →	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Period	2-zone fluorination									1-zone fluorination									Plutonium cleanup			
Gas flow path	Once through																		Recycle			
Cumulative hexafluoride collection, % of charge				39				75		80				95								
Fluorine addition point	Side inlet			Side inlet				Side inlet											Bottom inlet			
Flow rate through fluorinator bottom inlet, cfm	~1.8									~2.0									~1.6			
Flow rate through fluorinator side inlet, cfm	~0.6									Side inlet closed												
Average concentration, vol.% Fluorine in entering gas, vol %*	~6			~11				~9		~6												
Oxygen in entering gas, vol %†	~23			~13		~17			~22						O_2 Off							
Fluorine concentration of process off-gas, vol.%	Variable but below 10										Increasing, 10 to ~90						~90					
Nominal temperature, °C → Pellet bed	Gradient 400–450							450														
→ Alumina bed	450													450 to 500		500		500 to 550		550		

*Fluorine flow rate is divided by the sum of the side and bottom flow inputs to obtain this value.

†Oxygen flow rate in the bottom input stream is divided by the total flow rate into the bottom inlet to obtain this value.

FLUORINATION OF UO_2 FUEL WITH BrF_5

Workers at ANL are investigating a method for effecting the separation of uranium from plutonium based on the selective fluorination of uranium to volatile UF_6 by bromine pentafluoride. The plutonium, which remains nonvolatile, is recovered as PuF_6 in a subsequent step by fluorination with fluorine. Since the direct reaction of sintered UO_2 does not proceed readily with BrF_5 alone or in mixtures with oxygen at temperatures up to 400°C, the oxide fuel is pulverized to $U_3O_8-PuO_2$ powder by reaction with oxygen prior to fluorination. Demonstration tests with UO_2-PuO_2 fuel on the process cycle $O_2-BrF_5-F_2$ are being carried out in a 2-in.-diameter fluid-bed reactor.[3] In these tests the pellets are pulverized with 20 vol.% oxygen for 2 to 4 hr at 450°C. The oxide fines are reacted with approximately 10 vol.% BrF_5 for 2 to 3 hr at 400°C to form volatile UF_6 and nonvolatile PuF_4. Fluorination of plutonium to PuF_6 is carried out by recycle fluorination with 90 vol.% fluorine for 1 hr at 450°C, 3 hr at 500°C, and 8 hr at 550°C. The course of uranium and plutonium re-

moval during both fluorination steps, determined by analyses of samples from the fluidized alumina bed, is shown in Fig. III-6. Approximately 99% of the uranium was converted to UF_6 during the initial 1.75 hr of fluorination with BrF_5. During the subsequent 1.25 hr, the uranium concentration in the alumina bed decreased to 0.051 wt.%, corresponding to conversion of 99.8% of the initial uranium to UF_6. The concentration of both uranium and plutonium in the final bed was 0.008 wt.%.

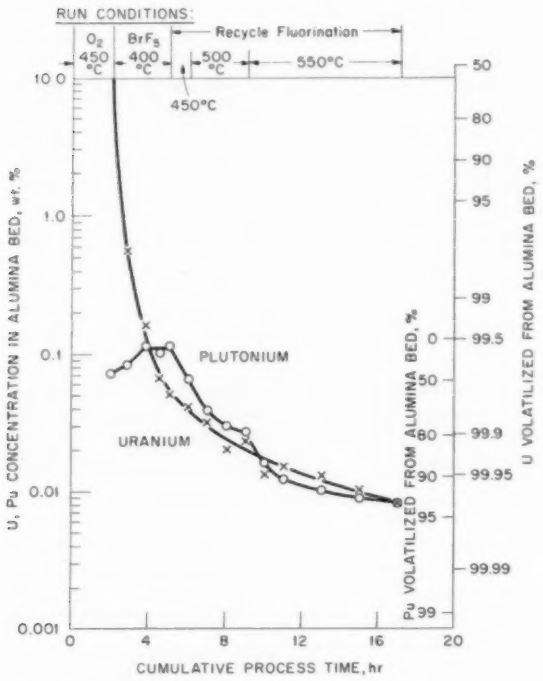


Fig. III-6 Uranium and plutonium concentrations in alumina fluidized bed.[3]

DESIGN OF EQUIPMENT FOR FLUID-BED FLUORIDE-VOLATILITY PROCESSES

A pilot-scale alpha–gamma facility is being constructed at CEN to study the remote chemical processing of spent-ceramic-fuel materials by fluidization techniques. Principal process equipment in the facility includes a fluid-bed reactor for fluorinating sintered oxide fuel, a series of condensers for collecting volatile fluorides, a NaF trap, a caustic scrubber, and a vessel for collection of the alumina-bed material and nonvolatile fission products. A discussion of the flow and handling of material within the facility appears in Ref. 14. Details of recent work on the development and testing of ventilation scrubbers, condensers, filters, and analytical methods for detecting trace constituents in gas streams are given in recent quarterly reports.[10,15,26] In a recent report Schmets, Heremans, and Pierini[27] have discussed the design philosophy of the facility being constructed at CEN.

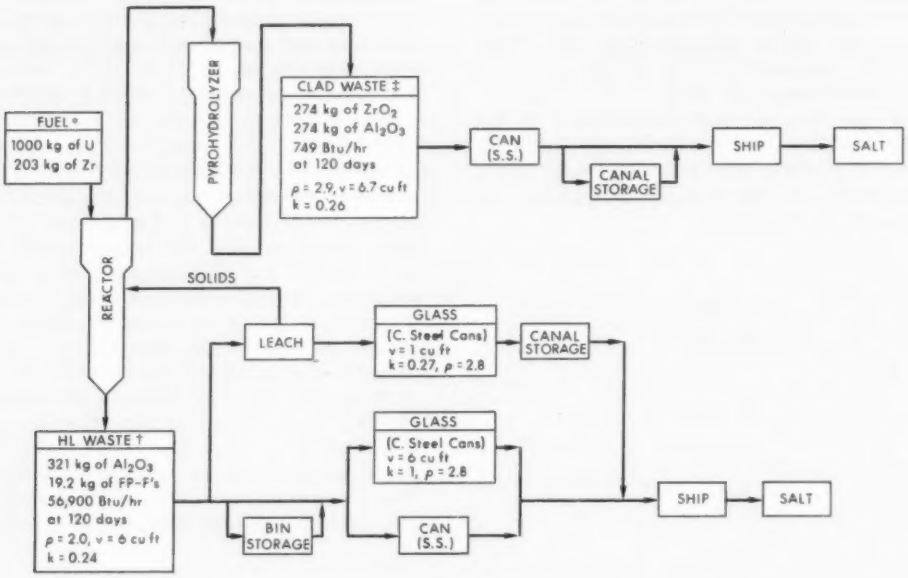
In connection with the plan of the U. S. Atomic Energy Commission (AEC) to construct a hot engineering-scale pilot plant at Oak Ridge National Laboratory to demonstrate the separation of plutonium and uranium from low-enrichment fuels, workers at Oak Ridge Gaseous Diffusion Plant (ORGDP) have been concerned with the preparation of conceptual plant studies and the definition of problem areas associated with process technology, including component development and testing of process equipment. Details of the ORGDP studies have been published recently in a summary report.[28] The report reviews work on the following subjects: theoretical aspects of UF_6–PuF_6–fission-product fluoride distillation, design of a reactor for producing BrF_5 from BrF_3, condenser systems for collection of BrF_5–UF_6 mixtures, corrosion tests, criticality calculations for the UF_6–NaF system, and evaluation of compressors.

Waste Disposal for Fluoride-Volatility Processes

Integral with the development of fluid-bed fluoride-volatility processes is the need to establish effective measures for the safe and economic disposal of the solid wastes generated in the process, such as the aluminum oxide fluid-bed material. Two methods for treating the aluminum oxide bed are being studied at BNL:[1] (1) leaching of the fission products from the bed, followed by fixation of the extracted fission products into a stable solid medium, and (2) encapsulation of the bed in low-melting materials (300 to 800°C). Leaching studies using simulated fission products indicated that a concentrated phosphoric acid leach was capable of removing 95 to 100% of the fission products from an aluminum oxide bed. This solution can then be converted directly to a phosphate type glass.

Several experiments were carried out to encapsulate alumina-bed particles. Satisfactory results were achieved with lead silicate glasses that exhibit a thermal conductivity approximately 10 times that of bulk aluminum oxide.

Suddath and Blomeke[29] have prepared an economic analysis of several methods for managing the disposal of solid wastes generated in fluid-bed fluoride-volatility processes. The alternative methods are illustrated in Fig. III-7 for, as an example, the processing of Zircaloy-2-clad UO_2 fuel. Results of the analysis indicated that there is not a clear-cut economic incentive to convert the solids to glasses or to leach fission products from the solids. A more attractive alternative is to encapsulate the solids after several years' bulk storage and ship the containers to a salt mine for final disposal.



*UO_2 fuel rods 0.369 in. in diameter with Zircaloy cladding 0.0215 in. thick; 21,000 Mwd/metric ton.

†Based on Al_2O_3/fuel = 1.2 and use of beds for 5 cycles.

‡Assumes the presence of 1% of fission products plus 5300 curies of induced ^{95}Zr–Nb activity per metric ton of uranium; v = volume, cubic feet; ρ = density, grams per cubic centimeter; k = thermal conductivity, British thermal units per hour per foot per degree Fahrenheit.

Fig. III-7 Managment of wastes from fluoride-volatility processing of Zircaloy-2-clad UO_2 fuel.[29]

Preparation and Properties of Fluorides

SORPTION OF URANIUM HEXAFLUORIDE

Decontamination of UF_6 produced by fluoride-volatility techniques can be accomplished by a sorption–desorption cycle in a bed of NaF pellets. Uranium hexafluoride reacts with sodium fluoride to form either $UF_6 \cdot 2NaF$ or $UF_6 \cdot NaF$ depending upon the partial pressure of UF_6 and the temperature. Smiley, Brater, and Pashley[28] at ORGDP have evaluated the use of NaF as a sorbent for UF_6 in prototype systems. Sorption of UF_6 is markedly affected by gas velocity. Increasing the velocity through a packed bed of NaF pellets from 0.08 to 0.19 ft/sec resulted in a decrease in the effective sorptive capacity* from 0.31 to 0.15 lb of UF_6 per pound of NaF. Sorptive capacities were essentially the same for cylindrical and annular traps.

Criticality calculations were made for NaF traps used for the sorption of UF_6. It was assumed that $UF_6 \cdot NaF$ and $NaF \cdot HF$ complexes would be present in the equipment. Initial calculations were made for UF_6 containing 6% ^{235}U. The maximum allowable diameter was about 24 in., considering finite length and 30-cm water reflection.[28]

The use of a bed of MgF_2 pellets for removing trace quantities of volatile technetium, neptunium, molybdenum, and vanadium fluorides from UF_6 gas streams was reported by Golliher.[30] Beds of MgF_2 pellets, 0.09 to 0.25 in. in diameter, at 90 to 120°C are highly effective in removing these fluoride impurities from large quantities of UF_6.

The use of other solid fluorides as sorbents for the removal of volatile fluoride impurities from UF_6 gas streams is being studied at ORGDP.[31] In tests in which NbF_5 was vaporized into a stream of UF_6 and the mixture immediately passed through sorbent traps, it was found that the concentration of NbF_5 in the UF_6 could be reduced from several hundred parts per million to less than 1 ppm by passing the gas through either NaF at 400°C or MgF_2 at 120°C. The sorptive capacities of both materials appeared high, but a low-melting compound formed in the NaF trap which eventually plugged the trap. Sodium fluoride pellets at 344°C were effective in reducing the concentration of RuF_5 in UF_6 to less than 1 ppm. Although the capacity of MgF_2 or NaF for removal of TiF_4

*Sorptive capacity is defined as the pounds of UF_6 sorbed per pound of NaF when the concentration of UF_6 at the outlet of the NaF trap first exceeds 1 ppm.

from UF_6 has not been established, it appears that either material can remove small quantities of TiF_4 from UF_6.

COMPLEX FLUORIDES OF URANIUM AND NEPTUNIUM

The fluorides of uranium form a complete series of complex compounds with alkali-metal fluorides. It has been recently reported[32] that UF_5 forms complex fluorides with the alkali fluorides KF, RbF, and CsF by reaction of uranium metal, alkali fluoride, and UF_4 at 1000°C in a sealed chamber. Compounds were found with $MF:UF_5$ ratios of 1:1 for $M = Na^+$, K^+, Rb^+, or Cs^+; 2:1 (except for Na^+); and 3:1 (except for Na^+). The $3KF \cdot UF_5$ crystalline phases are of face-centered cubic symmetry and are isomorphous with the $3KF \cdot UF_4$ and $3KF \cdot UF_5$ analogs with nearly identical cell parameters.

Asprey et al.[33] have prepared alkali fluoride complexes of pentavalent neptunium by treating alkali fluoride–NpF_4 compounds with fluorine at 5 psig for 8 to 16 hr at 250 to 300°C. The compounds $CsNpF_6$ and Rb_2NpF_7 were prepared. X-ray diffraction data showed that $CsNpF_6$ is rhombohedral, isostructural with $CsUF_6$, and that Rb_2NpF_7 is monoclinic, isostructural with Rb_2PuF_7 and K_2TaF_7.

PROPERTIES OF VOLATILE FLUORIDES

Osborne and associates[34] have measured several thermodynamic properties of MoF_6 at temperatures between 4 and 350°K. The enthalpy change for the solid–solid transition at 263.48 ± 0.02°K is 1953.3 ± 2.0 cal/mole, and the enthalpy of fusion at the triple point, 290.73 ± 0.02°K, is 1034.2 ± 1.0 cal/mole. The vapor pressure of MoF_6 at temperatures between 291 and 320°K is represented by the equation

$$\log P \text{ mm Hg} = -2047.15/T - 4.28004 \log T + 20.19354$$

The standard entropy of the gas at 298.15°K is 83.75 ± 0.10 cal/(deg)(mole).

A program is under way at ANL to determine thermodynamic properties of substances of interest in the fields of high temperature and atomic energy by fluorine-bomb calorimetry. Recent work[35] has concerned the measurement of the enthalpies of formation of SF_6, SeF_6, and TeF_6 by combustion of the elements (rhombic sulfur, hexagonal-black selenium, and metallic tellurium) in fluorine. The derived thermal data for the formation of the gaseous hexafluorides at 25°C are:

	SF_6	SeF_6	TeF_6
Energy of formation $\Delta E_f^\circ = \Delta E_r^\circ$, kcal/mole	$-290.5_2 \pm 0.2_4$	$-265.7_7 \pm 0.1_4$	$-326.0_2 \pm 0.5_6$
Enthalpy of formation ΔH_f°, kcal/mole	$-291.7_7 \pm 0.2_4$	$-266.9_5 \pm 0.1_4$	$-327.2_6 \pm 0.5_6$
Entropy of formation ΔS_f°, cal/(deg)(mole)	−83.36	−80.47	−76.94
Gibbs energy of formation ΔG_f°, kcal/mole	$-266.9_2 \pm 0.2_4$	$-242.9_6 \pm 0.1_4$	$-304.2_6 \pm 0.5_6$

In connection with this study, thermodynamic properties of SF_6, SeF_6, and TeF_6 in the ideal-gas states were calculated[35] employing the rigid rotator–harmonic oscillator approximation over the temperature range 0 to 1500°K. In other work Abramowitz and Levin[36] have determined Coriolis zeta constants for SF_6 and TeF_6. Thakur and Rai[37] have published the results of calculations of the force constants for 13 octahedral hexafluoride molecules.

Other properties of volatile fluorides which have been recently reported in the literature are: self-diffusion of uranium hexafluoride;[38] measurements of the binary diffusion coefficients of UF_6 in several gases;[39] the absorption spectrum of neptunium hexafluoride;[3,40] the infrared spectrum of ReF_7 vapor and Raman spectrum of ReF_7 liquid;[41] and the infrared spectrum of niobium pentafluoride.[42]

Volatility Processing of Fuel and Blanket of a Molten-Salt Breeder Reactor

By W. J. Mecham

At ORNL a molten-salt breeder reactor (MSBR) system is being developed. In the system concept the reactor employs molten fluoride salts for both core and blanket. Continuous processing is provided by a combination of fluoride-volatility and salt-distillation techniques. The processing scheme is shown in Fig. III-8. A detailed description of the processing steps and plant equipment was given previously.[43] Similar processing will be provided for fuel of the single-region 10-Mw reactor of the Molten Salt Reactor Experiment (MSRE).

Investigations of the vapor pressures of the fluoride melts are being made to determine the vapor composition in the $LiF-BeF_2$ salt system and to determine rare-earth concentrations in the salt-distillation step used for decontamination of the fuel salt. Only preliminary results have been obtained thus far.[44]

Continuing studies of densities of molten fluoride mixtures has confirmed the rule of additive molar volumes as an accurate method of predicting densities of mixtures. (An exception is the system $NaF-UF_4$, for which positive deviations as great as 6% were observed.) A set of empirical molar volumes of fluorides is given in Table III-3. For estimating a density expression of the form

$$\rho = a + bt \tag{1}$$

the following equation is first solved for densities at two temperatures by using the equation

$$\rho_t = \frac{\sum_{i=1}^{n} (N_i M_i)}{\sum_{i=1}^{n} [N_i V_i(t)]} \tag{2}$$

where N_i and M_i are the mole fraction and gram-formula weight of component i, and $V_i(t)$ is the molar

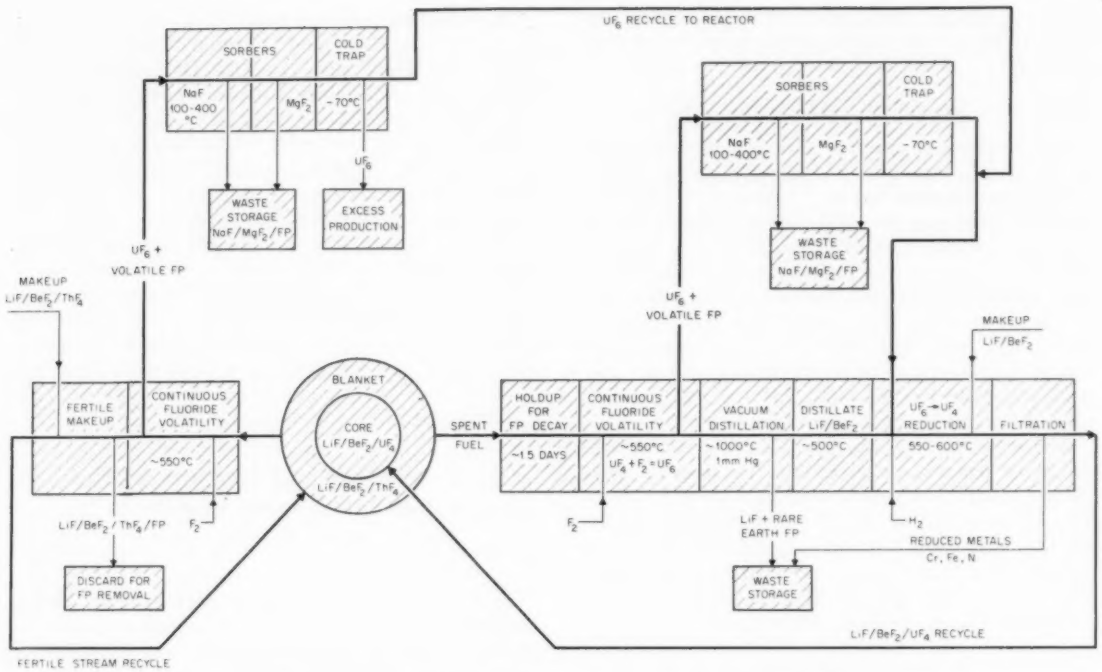


Fig. III-8 MSBR core and blanket stream processing scheme.[44]

volume of component i at temperature t. Molar volumes are substituted from Table III-3 at the two different temperatures to obtain the two values of ρ_t; since density is linear with temperature, substitution of the two pairs of values of ρ_t and t in Eq. 1 provides the solution for the constants a and b.

Table III-3 EMPIRICAL MOLAR VOLUMES OF FLUORIDES[44]

	Molar volume, cm³/mole			Molar volume, cm³/mole	
	At 600°C	At 800°C		At 600°C	At 800°C
LiF	13.46	14.19	AlF_3	26.9	30.7
NaF	19.08	20.20	YF_3	34.6	35.5
KF	28.1	30.0	LaF_3	37.7	38.7
RbF	33.9	36.1	CeF_3	36.3	37.6
CsF	40.2	43.1	PrF_3	36.6	37.6
BeF_2	23.6	24.4	SmF_3	39.0	39.8
MgF_2	22.4	23.3	ZrF_4	47	50
CaF_2	27.5	28.3	ThF_4	46.6	47.7
SrF_2	30.4	31.6	UF_4	45.5	46.7
BaF_2	35.8	37.3			

Examination of the heat-capacity measurements of molten fluorides indicated that the heat capacity per gram atom of melt is approximately 8 cal/°C. Hence an expression similar to that of Dulong and Petit may be used to estimate specific heats of fluoride melts. The expression is

$$c = \frac{8 \sum_{i=1}^{n} (N_i p_i)}{\sum_{i=1}^{n} (N_i M_i)} \qquad (3)$$

where c is the specific heat in calories per gram per degree Kelvin, p_i is the number of atoms in a molecule of component i, and N_i and M_i are the mole fraction and the gram-formula weight, respectively, of component i.

A new semitheoretical expression for thermal conductivity based on Bridgman's theory of energy transport in liquids has been developed. The expression is

$$k = \frac{13}{V^{2/3}} \mu \qquad (4)$$

where k is the thermal conductivity, V is the molar volume, and μ is the velocity of sound in the melt; all three variables should be in centimeter-gram-second units. The molar volume and velocity of sound are needed if Eq. 4 is to be used. Molar volume is easily estimated by the rule of additivity as outlined above. The velocity of sound may be estimated from thermodynamic quantities, using the expression

$$\mu^2 = \frac{[(C_p/C_V) - 1]C_p}{\alpha^2 TM} \qquad (5)$$

where C_p = molar heat capacity at constant pressure
C_V = molar heat capacity at constant volume
α = expansivity
T = absolute temperature
C_p/M = specific heat (and should be expressed in ergs per gram per degree Kelvin)

The ratio C_p/C_V varies between 1.2 and 1.35 for most fused salts (1.2 works quite well). The expansivity is the negative of temperature coefficient of density, divided by the density, i.e.,

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p$$

The estimation of α is made by using the additivity rule.

Investigations are being made of vacuum distillation as a way of separating fluoride components of the molten-salt fuel from rare-earth fission products, which are the major neutron poisons. In specific application to MSRE fuel, uranium is first removed by fluorination, and then the fuel solvent and residual fission products are fed at the distillation rate to a vacuum still charged with a $LiF-BeF_2-ZrF_4$ salt mixture at that composition which will yield the composition of fuel solvent as distilled overhead product. The rare-earth fission products concentrate in the still and are removed as required by buildup of heat or concentration of rare earths.

Distillation rates were studied in small-scale experiments in which 10-ml graphite cylinders served as still pots containing about 17 g of salt with a molten surface of 1 cm^2. Results are presented in Fig. III-9.

As shown in Fig. III-9, the MSRE fuel solvent distills at higher rates than pure LiF. At present there is no satisfactory explanation of why LiF distills at only $^1/_{10}$ of the theoretically predicted rate. The composition of the fuel solvent is $LiF-BeF_2-ZrF_4$, 65–30–5 mole %. Other salt compositions being considered are also expected to distill at rates above that of LiF, with the possible exception of ThF_4-bearing salts, which are being studied separately.

Neodymium (as NdF_3) was added at levels of 2200 and 22,000 ppm to the fuel solvent, and aliquots of solvent were distilled overhead. Mean values from several experiments in the temperature range of interest (about 1000 to 1100°C) showed neodymium concentrations in overhead product that were factors of the order of 100 lower than concentrations in the charge.

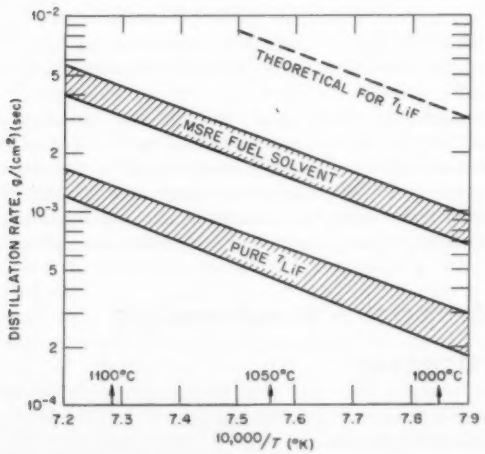


Fig. III-9 Observed distillation rate vs. temperature.[44]

Studies of the removal of rare earths from a molten fluoride solvent and their dissolution in molten metals have been directed toward the development of a liquid–liquid extraction process for removing rare-earth fission products from molten-salt reactor fuels. Such extractions would be done in the absence of uranium, which is removed in a previous fluorination step. Results of extractions of rare earths from $LiF-BeF_2$ salt into a molten bismuth–lithium mixture are shown in Fig. III-10. In this extraction lithium reduces the rare-earth fluorides to metal.

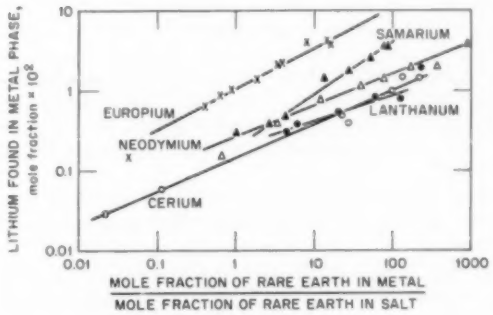


Fig. III-10 Effect of lithium concentration in metal phase on the distribution[44] *of rare earths between $LiF-BeF_2$ (66–34 mole %) and bismuth at 600°C.*

Studies are being made of oxide solubilities in fluoride salts of interest in the MSRE program. It is important that precipitation of fuel components does not occur in the reactor; accordingly the tolerance of salt for oxide in solution is a property of interest. The results are summarized in Figs. III-11 and III-12 for the fuel salt $LiF-BeF_2-ZrF_4$ (65–30–5 mole %) and the flush salt $LiF-BeF_2$ (67–33 mole %). The plot of oxide concentration as a function of ZrF_4 concentration in Fig. III-11 shows a minimum at a ZrF_4 concentration equivalent to 15 wt.% fuel salt in flush salt. This salt (with minimum oxide tolerance) is shown together with the fuel salt and flush salt in Fig. III-12, where oxide tolerance is plotted as a function of temperature.

Another processing step under study is the removal of protactinium from molten fluorides. In the conceptual molten-salt breeder reactor, fissionable ^{233}U will be recovered as the decay product of ^{233}Pa. Since equilibrium concentrations of ^{233}Pa result in appreciable parasitic neutron absorptions, the advantage of thermal breeding could be realized to a greater extent by removing ^{233}Pa from the reactor. This advantage can be realized whether or not the

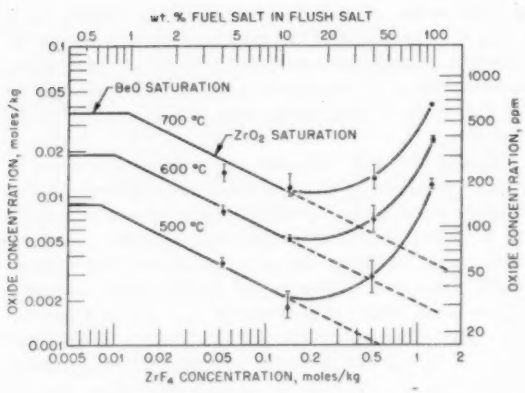


Fig. III-11 Oxide concentration required to produce precipitation of BeO or ZrO_2 from simulated MSRE flush-salt–fuel-salt mixtures.[44]

^{233}U is removed with the ^{233}Pa. For a two-zone breeder reactor, the ^{233}Pa and ^{233}U probably would be removed from the blanket together, whereas for a single-zone reactor only the ^{233}Pa would be removed.[44]

Small-scale experiments indicated that it is possible to remove protactinum from molten fluoride solutions simulating the blanket of the MSBR. The removal was accomplished by a process that appears to be surface precipitation of protactinium on beryllium oxide or thorium oxide particles. Protactinium was removed from molten mixtures of $LiF-BeF_2-ThF_4$ (67–18–15 mole %) by the addition of 1 to 2 wt.% of solid beryllium oxide or thorium oxide. The removal efficiency[45] was high when the initial concentration of protactinium was either in the range 1 to 2 ppb or 50 to 75 ppm.

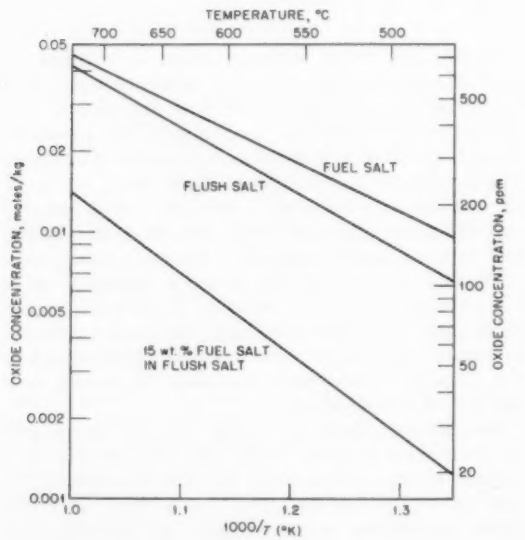


Fig. III-12 Temperature dependence of oxide tolerance: (1) in flush salt (BeO-saturated), (2) in flush-salt–fuel-salt mixture of minimum oxide tolerance and (3) in fuel salt.[44]

Uranium was successfully removed from solution in molten fluorides by use of a similar procedure. Approximately 2000 ppm uranium was precipitated from molten $LiF-BeF_2-ThF_4$ (67–18–15 mole %) by the addition of 3 wt.% of beryllium oxide. Comparable results were also obtained using thorium oxide as the precipitant.[45]

In the fluoride fuel mixture of the MSRE, sufficient ZrF_4 has been added to accommodate gross oxide contamination without loss of uranium from solution as UO_2. Earlier studies had demonstrated that UO_2 would not precipitate at 700°C from the solvent, $LiF-BeF_2$ (66–34 mole %) with added UF_4 and ZrF_4, until the concentration ratio of ZrF_4 to UF_4 dropped below about 1.5. Therefore a preliminary study was made of the precipitation of PaO_2 from a fluoride mixture known to have ZrO_2 as the stable oxide phase.[44]

In these preliminary tests about 1 mc of ^{233}Pa was included in a salt mixture containing $LiF-BeF_2$ (66–34 mole %) and added ZrF_4 equivalent to 0.5 mole of zirconium per kilogram of salt. Adding ZrO_2 in small increments accomplished the removal of the protactinium. Experimental results were correlated by the expression of the form

$$\frac{1}{F} = 1 + D\left(\frac{W_{ZrO_2}}{W_{salt}}\right)$$

where F = fraction of ^{233}Pa in liquid salt

$\left(\frac{W_{ZrO_2}}{W_{salt}}\right)$ = weight ratio of phases

D = Pa distribution coefficient

$$= \frac{\text{concentration of Pa in } ZrO_2 \text{ (solid) phase}}{\text{concentration of Pa in salt (liquid) phase}}$$

A constant value of $D = 237$ was found in tests in which up to about 60 g of ZrO_2 was added to 3.7 kg of salt.[44]

Studies are also under way of the removal of protactinium from molten fluorides by reduction processes. In preliminary tests at 600°C with trace quantities of ^{233}Pa, the protactinium was rapidly removed from synthetic blanket salt by contact with molten lead containing 0.1 wt.% thorium metal.[44]

Compact Pyrochemical Processes

By T. R. Johnson and R. K. Steunenberg

Pyrochemical processes, a class of nonaqueous procedures for the recovery and purification of par-

tially burned reactor fuels, are being developed for the processing of both ceramic (oxide and carbide) and metallic fuels. Most pyrochemical processes presently under investigation make extensive use of molten metals and salts as media in which separations are effected. The liquid metals are typically alloys of magnesium with copper, cadmium, or zinc, and the salts usually involve magnesium chloride that may be diluted with chlorides of alkali and other alkaline-earth metals. In other pyrochemical processes certain types of fuel are treated in the absence of a solvent.

Pyrochemical processes have certain technological and economic features that should be particularly beneficial in fast reactor fuel cycles. Among these features are: (1) the ability to accommodate short-cooled high-burnup fuels with a consequent reduction of out-of-reactor fuel inventories, (2) small process volumes that require a minimum of shielded space, (3) less restrictive criticality limits because of the absence of neutron-moderating materials, (4) compact, solid-waste streams, and (5) adaptability to small, on-site plants for one or a few reactors. In the case of metal fuels, expensive alloying agents can be recovered. Since these processes do not provide complete fission-product removal, all handling operations, including fuel refabrication, are performed remotely.

Processes for Future Fast Reactor Fuels

SALT-TRANSPORT PROCESSES

Pyrochemical processes that incorporate a salt-transport step for the recovery of uranium and plutonium and the separation of fission products from fast breeder reactor fuels are being investigated by Argonne National Laboratory (ANL). In the salt-transport step, fissile and fertile constituents of the fuel are transferred selectively from one liquid-metal solution (donor solvent) to other metal solutions (acceptor solvents). A molten-salt phase containing $MgCl_2$ serves as the carrier for the transfer of solutes between the liquid-metal solutions.

Processes of this type utilize simple, compact equipment. Volumes of the process solutions are small because not all the uranium or plutonium needs to be in solution at any one time. Salt-transport processes show promise of providing good fission-product removals together with high recoveries of uranium and plutonium. A conceptual process flow sheet that is currently under investigation was described in a previous review.[46] The initial step of the process is oxidative decladding of an oxide or carbide fuel, in which the fuel is separated from the cladding and the volatile fission products are collected. The oxides from the decladding step are reduced by a copper–10 wt.% magnesium alloy in the presence of a $MgCl_2$-based salt. In the reduction step the alkali, alkaline-earth, and rare-earth fission products remain in the salt phase, which also serves as a vehicle for the removal of solid MgO formed in the reduction reaction. The uranium, the plutonium, and the other fission products appear in metallic form in the copper–magnesium alloy. The uranium and plutonium are then separated from the noble- and refractory-metal fission products by a salt-transport separation. The copper–magnesium donor alloy and zinc–magnesium acceptor alloys are placed in mutual contact with a $MgCl_2$-based carrier salt. The uranium transfers selectively to a zinc–high magnesium alloy, and the plutonium, to a zinc–low magnesium alloy. The fission products (zirconium through antimony) remain in the copper–magnesium donor alloy. The two zinc–magnesium solutions are retorted to recover metallic uranium and plutonium that are then reconverted to oxides or carbides.

Copper–magnesium alloys are favored for use in the reduction step because the separation factor for rare earths and plutonium between the salt and metal phases is large. Distribution coefficients[47] of plutonium and cerium between molten $MgCl_2$ and liquid copper–magnesium alloys were measured at 800°C. The magnesium content of the alloy was varied from 6 wt.% to 70 wt.%. The cerium–plutonium separation factor

$$\frac{(\text{Wt.\% Ce in salt})}{(\text{Wt.\% Pu in salt})} \Big/ \frac{(\text{wt.\% Ce in alloy})}{(\text{wt.\% Pu in alloy})}$$

varied from a value of about 310 for a copper–6.5 wt.% magnesium alloy to one of about 38 for a copper–70 wt.% magnesium alloy. The cerium–uranium separation factors were calculated to be about 2230 for the copper–6.5 wt.% magnesium alloy and about 96 for the copper–70 wt.% magnesium alloy.

Since the molten salt from this step is a waste stream containing MgO and fission products, it is desirable that the concentration of fissile elements be low so as to minimize losses. The amount of salt employed in the reduction step cannot be selected solely on the basis of rare-earth removals and plutonium recoveries in the extraction process. The amount of MgO generated during the reduction step places a lower limit on the amount of salt used since a salt containing more than about 12 wt.% MgO becomes viscous and difficult to transfer. A low $MgCl_2$ concentration lowers the oxidizing power of the salt phase and decreases the equilibrium concentration of all reducible constituents (uranium, plutonium, and rare-earth elements) in the salt. However, reduction rates of uranium oxides in liquid-metal–salt systems have been found to decrease with decreasing $MgCl_2$ concentration. Optimization of the reduction step with respect to these conflicting requirements of oxide reduction and rare-earth–plutonium partition was discussed in the preceding issue of *Reactor Fuel Processing*.[48]

So that regions of practical operating conditions could be defined,[47] distribution coefficients of cerium, uranium, and plutonium between a copper–6 wt.% magnesium alloy and molten $NaCl–CaCl_2–MgCl_2$

mixtures were measured at 800°C. The NaCl:$CaCl_2$ mole ratio was kept at unity while the $MgCl_2$ content was varied from about 1 to 100 mole %. Although the distribution coefficients all increased with increasing $MgCl_2$ concentration in the salt (see Fig. III-13), the cerium–uranium separation factor remained essentially constant. The cerium–plutonium separation factor increased from about 200 at 1 mole % $MgCl_2$ to 310 at 100 mole % $MgCl_2$. These results indicate that good separations can be obtained at low, as well as high, $MgCl_2$ concentrations.

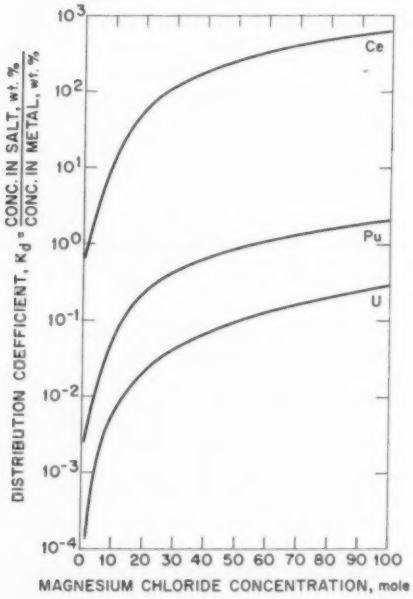


Fig. III-13 Distribution[47] of cerium, plutonium, and uranium between molten $CaCl_2$–NaCl–$MgCl_2$ and copper–6 wt.% magnesium alloy at 800°C.

The volume of waste salt from the reduction step can be decreased by recycling the salt extractant. Before the salt can be reused, the rare-earth elements must be stripped from the salt phase by contacting it with a strong reducing agent, such as a zinc–magnesium alloy, and the solid MgO must be removed. A sample of salt that contained MgO from a typical reduction of uranium oxide was examined.[49] The suspended particles of MgO had an average size of about 2 μ and a size range from 1 to 5 μ. When salt containing suspended MgO was held at 500°C for 6 hr, no significant change was found in the average particle size. The MgO settled rapidly and formed a clearly defined layer. The supernatant salt contained 0.25 wt.% MgO, and the settled layer, 22 wt.% MgO. The $MgCl_2$ concentrations of the liquid in both layers were equal, indicating that $MgCl_2$ had not been removed from the liquid salt.

As the transfer of uranium in a salt-transport process nears completion, the copper–magnesium donor alloy becomes unsaturated with metallic uranium and the uranium concentration begins to decrease. Since the distribution coefficient[50] of uranium strongly influences the rate of uranium transfer, the effect of decreasing uranium concentration on its distribution coefficients between molten $MgCl_2$ and copper–magnesium alloy was measured at 750, 800, and 850°C. For uranium concentrations varying from about 0.1 wt.% to the saturated values (2.1 wt.% at 750°C and 7.6 wt.% at 850°C), the distribution coefficients were independent of the uranium concentration in the metal phase. The magnesium content of the alloy corresponded to the copper-saturated liquidus composition in the copper–magnesium phase diagram at the temperature of the measurement. The results were as follows:

Temperature, °C	Mg content of liquid-metal phase, wt.%	Distribution coefficient*
750	9.4	0.22
800	8.0	0.29
850	6.8	0.42

*Distribution coefficient (K_d) = (wt.% uranium in salt phase)/(wt.% uranium in metal phase).

Cadmium–copper–magnesium alloys are being considered as an alternative to copper–magnesium alloys for use as a donor solvent. The ternary alloy offers the possibility of lowering the operating temperature of the salt-transport process from 800 to 600°C. The distribution coefficients[49] of uranium, plutonium, and cerium between a 50 mole % $MgCl_2$–30 mole % NaCl–20 mole % KCl salt and liquid cadmium–copper–magnesium alloys were measured at temperatures of 600 and 700°C. The alloy consisted of equal weights of cadmium and copper, and magnesium at concentrations ranging from 0.4 to 18 wt.%. The results indicated that such an alloy containing about 2 wt.% magnesium could be used as a donor solution at temperatures of 650 to 700°C. The transport characteristics of uranium and plutonium are about the same as for the binary copper–magnesium alloy. However, the ternary alloy has the disadvantages that it would be more difficult to control the magnesium content of the alloy during the transport step and that the plutonium–rare-earth separation in the reduction step would be somewhat less efficient. Nevertheless, the engineering advantages of operation at a lower temperature may outweigh these disadvantages.

A laboratory-scale experiment[47] has shown that uranium can be transported satisfactorily from a 60 wt.% copper–30 wt.% cadmium–2 wt.% magnesium donor solvent through a 50 mole % $MgCl_2$–30 mole % NaCl–20 mole % KCl salt phase to a 60 wt.% magnesium–40 wt.% zinc acceptor alloy at 700°C.

A pilot-plant-scale experiment was conducted[50] in which uranium was separated from various refractory

and noble-metal fission-product elements by the salt-transport method. To prepare the feed to the salt-transport step, workers added unirradiated UO_2 to molten 47.5 mole % $MgCl_2$–47.5 mole % $CaCl_2$–5 mole % CaF_2 and reduced it at 830°C by liquid copper–15. wt.% magnesium alloy to which ruthenium, molybdenum, zirconium, and palladium were added as the metals. The salt containing the MgO by-product of the reduction was removed from the system via a transfer line. The uranium in the molten copper–5.5 wt.% magnesium donor alloy was transferred incrementally to a molten magnesium–35 wt.% zinc acceptor alloy by cycling liquid $MgCl_2$ between the two alloys in adjacent vessels. Prior to each transfer the salt and metal phases were mixed to promote chemical equilibrium, and then the phases were allowed to separate by settling. Nearly 99% of the uranium was transported to the magnesium–zinc acceptor alloy. After the precipitated uranium product was washed with a magnesium–30 wt.% zinc alloy, the uranium product was dissolved in a zinc–13 wt.% magnesium solution that was retorted to recover a metallic uranium product. The following overall removals of fission-product elements from the uranium were achieved: zirconium, 98.5%; palladium and molybdenum, 99.9%; ruthenium, 99.99%. The single wash of the uranium product removed more than 90% of the palladium, molybdenum, ruthenium, and copper that had transferred with the uranium. However, the zirconium that had transferred had co-precipitated with the uranium and was not removed by the wash.

Results of work at ANL on containment materials for pyrochemical processes were summarized recently in a paper presented at the 15th Annual AEC Corrosion Symposium.[51] The principal metal–salt systems under investigation have been zinc–magnesium, cadmium–zinc–magnesium, and copper–magnesium liquid-metal phases in contact with $MgCl_2$-based salts containing additives such as NaCl, KCl, $CaCl_2$, and MgF_2. In most cases uranium was added to simulate the presence of discharged reactor fuel.

In the zinc–magnesium–uranium/halide-salt system at 800°C, tungsten exhibited excellent resistance to the combined attack of metal and salt. A molybdenum–30 wt.% tungsten alloy had adequate corrosion resistance for many applications but was slowly attacked by leaching of the molybdenum. Tantalum was attacked by zinc at 800°C by intergranular penetration and by the formation of tantalum–zinc intermetallic compounds.

Ferritic steels proved to have adequate resistance to corrosion by cadmium–zinc–magnesium–uranium/chloride-salt systems when the zinc content of the alloy was less than 20 at.% and the temperature was below 650°C. Tantalum, tungsten, and several ceramic materials were also resistant to this system.

The copper–magnesium/halide-salt systems have been contained successfully in cast iron, CB-30 (a stainless-steel alloy), and Croloy 16-1. However, there is a possibility that the solute uranium may react with carbon in the steels or with the iron to form low-melting iron–uranium compounds.

Additional progress at ANL on the development of engineering equipment and components for pyrochemical processes has been reported. A topical report[52] was issued on the development of a device to determine liquid levels of molten metals. The interface between a liquid metal and a gas or liquid salt was located by the change in mutual inductance of a bifilar coil. The presence of a conducting substance, such as a liquid metal, causes a change in the coil inductance that can be measured as a change in the voltage induced in the secondary coil when a high-frequency voltage is applied to the primary coil. Probes that are about 5 and 14 in. long have been calibrated in liquid cadmium, bismuth, and sodium over various temperature ranges up to 700°C. The output signal was only slightly affected by differences in the resistivities of these metals but was influenced significantly by the temperature. The average deviation in the liquid-level measurements was 2 to 3% of the probe length.

Studies at ANL of extraction rates between liquid-metal and molten-salt solvents were summarized at a recent A.I.Ch.E. Regional Symposium.[53] Mass transfer rates in a variety of liquid-metal–salt systems have been measured and correlated. It is expected that this information together with the increasing availability of materials for high-temperature use will lead to significant improvements in the design of high-temperature process equipment. The review covered investigations of the dissolution of a uranium sphere in flowing cadmium,[54,55] studies of mixing power and mass transfer rates in agitated systems consisting of a single metal phase and two-phase salt–metal mixtures, and preliminary work on packed extraction columns for liquid-metal–molten-salt systems.

Several equipment components[49] were subjected to performance tests in a loop through which a molten salt containing $MgCl_2$ was circulated at temperatures of 500 to 550°C. The components included a centrifugal pump, an orifice flowmeter, a bellows-sealed valve, a freeze valve, and a null type pressure gauge that employed a mutual inductance device. After 160 hr of operation at an average flow rate of 0.8 gal/min, little or no corrosion of the type 304 stainless-steel tubing could be detected.

Processes for Current Reactor Fuels

EBR-II FUEL CYCLE FACILITY AND OPERATIONS

The fuel cycle for the Second Experimental Breeder Reactor (EBR-II) was described previously.[56] In this cycle the metallic alloy fuel discharged from the reactor is decanned mechanically, processed by melt refining, formed into fuel pins by injection casting, reassembled, and returned to the reactor. The op-

erations that make up the fuel cycle are performed remotely, and most of them take place in an inert-atmosphere, shielded cell. The EBR-II Fuel Cycle Facility is presently operating on a routine production basis.

The melt-refining process is a pyrochemical procedure used to effect partial decontamination of the fuel alloy. The chopped fuel pins are melted in a zirconia crucible, and the molten metal is liquated at a temperature of 1400°C for about 3 hr. Volatile fission products are evolved from the melt as gases, which are collected. The alkali, alkaline-earth, and rare-earth fission products are removed from the metal through selective oxidation by the zirconia crucible. Noble- and refractory-metal fission products are not removed by melt refining and are retained in the fuel alloy at equilibrium concentrations. When the molten alloy is poured from the crucible at the conclusion of the melt-refining treatment, 5 to 10% of the metal together with oxides of the fission products remain in the crucible in the form of a skull. A process for the recovery of uranium from melt-refining skulls is described in the following subsection. Pouring yields in the melt-refining process have continued to average 93% with little or no difference in the yields obtained from irradiated fuel and those from unirradiated or recycled fuel.[57]

Studies have been made to determine the time and temperature requirements for melt refining under plant conditions.[58] At 1400°C the removals of fission-product barium, lanthanum, cesium, and iodine from the fuel were greater than 99.5%, and they did not change appreciably with liquation periods varying from 0.25 to 4.0 hr. However, the removal of cerium dropped from 99% to about 80 to 85% when the liquation time was decreased from 2.5 hr to 0.25 hr. Several 2-hr runs[57] were made in which the liquation temperature was varied between 1300 and 1400°C. The removal of cerium decreased from 99% at 1400°C to 89 to 96% at 1350°C and was still lower at 1300°C. The removals of barium and cesium were unaffected when the temperature was decreased from 1400 to 1350°C, but at 1300°C the removal of barium was 97% and that of cesium was 99.5%.

Most of the fuel-cycle operations associated with EBR-II take place in a shielded facility that has an argon atmosphere. Water, oxygen, and other reactive gaseous impurities are removed to prevent oxidation of the metallic fuels that are exposed to the cell atmosphere. The nitrogen concentration is maintained below 10 vol.% by purging the cell with fresh argon. Although this nitrogen level is acceptable in the EBR-II Fuel Cycle Facility, a method for removing nitrogen may be desirable in other future installations. Kyle, Arntzen, and Coleman[59] have described the design and operation of a pilot-plant unit for removing nitrogen from argon. The system employed titanium metal sponge at 900°C as a gettering agent for the removal of nitrogen. The unit was operated for a period of 1800 hr at a flow rate of 10 cfm of argon that contained 100 to 1000 ppm nitrogen. All the equipment items, with the exception of a rotary-lobe blower that developed leaks in the shaft seals, operated well. The usefulness and relative economy of titanium gettering for nitrogen removal were demonstrated by the conversion of 40% of the metal sponge to titanium mononitride. Since oxygen, water, and carbon dioxide inhibit the titanium–nitrogen reaction, these impurities must be removed from the gas by other means.

Operations in the EBR-II Fuel Cycle Facility are viewed through 5-ft-thick shielding windows that consist of four major glass components and a steel shutter that can be closed to decrease the exposure of the window to radiation when it is not in use. The ambient radiation level at the inside surface of some windows was expected to exceed 10^5 rads/hr. Eckels and Coleman[60] have calculated temperatures at various depths within the windows when they are exposed to a gamma intensity of 3.5×10^5 rads/hr, which is equivalent to a heat flux of 100 Btu/(hr)(sq ft). Transient temperature cycles were calculated for windows having the shutter alternately open for 8 hr and closed for 16 hr. For a cell temperature of 100°F, it was estimated that a maximum equilibrium temperature of 175°F would occur at a point 4.5 in. from the inside surface of the window when the shutter is open. The addition of a ¼-in.-thick glass cover plate on the inside of the window would increase the peak temperature to 215°F at a depth of 3.5 in. The purpose of the cover plate is to prevent window damage resulting from the internal discharge of a static electrical charge generated by the gamma radiation. These destructive discharges are initiated when a thick window is struck physically. The static charges tend to dissipate more rapidly as the temperature of the glass increases.

EBR-II SKULL-RECLAMATION PROCESS

The skull-reclamation process is being developed at ANL specifically to recover the 5 to 10% of the uranium charge that remains in the crucible after the melt refining of enriched-uranium fuel discharged from the EBR-II reactor. Although the skull-reclamation process for EBR-II fuel does not recover plutonium, much of the chemistry and technology being developed in the course of this work has potential utility for the processing of uranium and plutonium oxide, carbide, and metal fuels.

The steps in the skull-reclamation process are as follows:[61] (1) The uranium-bearing skull is oxidized, and the oxides are poured from the melt-refining crucible. (2) The oxide is suspended in a molten halide salt in a tungsten crucible, and the noble-metal fission products (molybdenum through cadmium) are removed by selective extraction with liquid zinc. (3) The uranium oxide in the salt phase is reduced by a magnesium–40 wt.% zinc alloy in which the metallic uranium product has a very low

solubility. The salt and the supernatant liquid metal, which contain the alkaline-earth and rare-earth fission products, are discarded as waste. (4) The uranium is dissolved in a zinc–14 wt.% magnesium solution that is transferred from the tungsten crucible to a mold. The resulting ingot is charged to a beryllia crucible where the zinc and magnesium are removed by vacuum distillation and the uranium is consolidated by melting.

The skull-reclamation process is being tested with unirradiated uranium in remotely operated, plant-scale equipment (~4.25 kg of uranium per batch). The equipment consists of a reduction furnace containing a large (14 in. in outside diameter by 26 in. high) tungsten crucible and a retorting furnace. The equipment and the operating procedures were described earlier.[62]

In a recent series of runs,[63] the noble-metal-extraction and oxide-reduction steps were conducted under more rigorous operating conditions than those used in earlier runs. The result was that higher removals of noble-metal fission products and better yields in the uranium oxide-reduction step were obtained. The addition of 10 mole % fluoride to the chloride salt between the noble-metal extraction and oxide-reduction steps resulted in uranium oxide-reduction yields[50] that exceeded 99%. Average values for the removal of fission-product elements added to the charge material were: molybdenum, 69%, ruthenium, 83%; cerium, 97%; zirconium, 60%. These removals are satisfactory for the EBR-II fuel cycle.

In 11 plant-scale experiments, the retorting apparatus and the beryllia crucibles performed satisfactorily. The retorting procedure entails distillation of the zinc and magnesium from the uranium product under vacuum (~10 torrs) at 650 to 750°C, followed by melting of the uranium to form a button. Two thixotropically cast beryllia crucibles (8 in. in outside diameter by 17 in. high) that had been used for a total of 14 runs were found to be in good condition.[64] A small amount of the liquid metal seeped through the crucibles, but this is considered to be a minor problem that can be solved by improved crucible fabrication techniques. Of the total quantity of zinc and magnesium distilled in these runs, only about 0.05% was unaccounted for. The uranium buttons were easily removed from the crucibles.

The uranium recoveries achieved in the plant-scale tests of the skull-reclamation process were about 93%. Since the melt-refining process yield is also about 93%, the overall uranium recovery for the combined melt-refining and skull-reclamation process in the EBR-II fuel cycle should be about 99.5%.

PROCESSES FOR MOLTEN FLUORIDE FUELS

In the two-region MSBR concept being investigated at ORNL, the blanket and core will require routine processing to remove fission products and to recover fissile material. The molten-salt core and blanket consist of UF_4 or ThF_4 dissolved in mixtures of LiF, BeF_2, and ZrF_4. Although fluoride-volatility methods are being considered most actively for the processing of this fuel, some attention is also being devoted to pyrochemical type processes.[65] The processing methods involve the reduction of undesirable constituents either electrolytically or by a metallic reductant and the assimilation of the contaminants into a separate solid or liquid phase. The possibility of removing contaminants through their interaction with beryllium to form insoluble intermetallic compounds is also being explored.

Experimental reduction–extraction studies were conducted in which various metallic reductants were contacted with a LiF–33 mole % BeF_2 salt phase containing small concentrations of lanthanum, gadolinium, and strontium. The metal and salt phases at temperatures in the range of 500 to 800°C were contacted by shaking for 0.5 to 4 hr. Some beryllium from the salt appeared in the metal phase. The stronger reductants, such as tin alloys containing high percentages of aluminum or lithium, were able to extract the added elements from the salt. However, the extraction resulted in the introduction of certain metal-phase constituents (tin or aluminum) into the salt, and black particles accumulated at the salt–metal interface. This black material was identified as beryllium–rare-earth intermetallic compounds of the form $Be_{13}M$, which are insoluble in both the salt and metal phases.

The possibility of exploiting the formation of beryllium intermetallic compounds as a means of removing fission products was investigated in a series of experiments in which LiF–BeF_2 salt mixtures were contacted with powdered beryllium at 550 to 600°C. From 60 to 90% of the trivalent rare earths were removed when 13 times the stoichiometric requirement of beryllium was used. Rare earths with a stable divalent state, such as europium, and the alkaline earths were not affected. Preliminary tests showed that more satisfactory results could be obtained through the use of lithium as a reductant to produce beryllium–rare-earth intermetallic compounds. Under these conditions the precipitated solids were granular and were easily separated by either filtration or sedimentation.

Other related work was reported by ORNL.[66] Fluoride salts (LiF–34 mole % BeF_2) containing about 0.01 mole % rare-earth fluorides were contacted with liquid bismuth–beryllium alloys at 600°C. Rare-earth removal from the salt phase exceeded 97%, and the reduced rare earths were only partially soluble in the metal phase, perhaps as a result of the formation of insoluble beryllium–rare-earth intermetallic compounds. The presence of lithium in the metal phase indicated that some reduction of LiF by the beryllium had occurred. Large percentages of cerium and neodymium were also reduced and removed from the fluoride salt by a lithium–bismuth alloy. The reduction of some BeF_2 by the lithium in this experiment

indicates that an observable equilibrium between lithium, beryllium, and their fluorides occurs in these liquid metal–molten fluoride systems.

Rapid recovery of ^{233}Pa from an MSBR will result in more economical production of fissionable ^{233}U by substantially decreasing the blanket inventory and equipment costs and by improving the neutron utilization. Therefore the chemical-processing development effort supporting the reference-design MSBR is concerned with the separation of protactinium from the blanket material (a $LiF-BeF_2-ThF_4$ mixture). The deliberate addition of oxide ion to precipitate an oxide of protactinium from the fuel of a single-region MSBR may provide the basis for protactinium recovery if the simultaneous precipitation of UO_2 can be avoided. Previous studies have demonstrated the chemical feasibility of oxide precipitation for recovering protactinium from a 67 mole % LiF–18 mole % BeF_2–15 mole % ThF_4 mixture that was proposed as the blanket of a two-region MSBR.[67] Tracer levels of protactinium were removed from a $LiF-BeF_2-ThF_4$ salt by the addition of ThO_2. Oxide contamination of the core material ($LiF-BeF_2-UF_4$) will not cause a loss of uranium from the solution if ZrF_4 is present at a concentration that is at least 1.5 times the UF_4 concentration since ZrO_2 precipitates preferentially under these conditions. When ZrO_2 was added incrementally to salt containing ^{233}Pa, the protactinium activity was removed from the salt either by solid-solution formation with ZrO_2 or by surface adsorption on the ZrO_2 powder. The fraction of protactinium removed from the salt was a linear function of the amount of ZrO_2 added.

Other experiments have shown that tracer levels of protactinium can be extracted from the blanket salt by a liquid-metal solution of thorium in lead or bismuth. The potential usefulness of this technique prompted measurements of the solubility of thorium in lead at temperatures of 400 to 600°C. The thorium solubility at 600°C was 1.85×10^{-2} mole %, and the heat of solution was 19 kcal/mole. The corrosion of nickel-free steels and niobium–1 wt.% zirconium alloy by lead in the absence and presence of molten fluoride salts was investigated using thermal convection loops.[68] Although the niobium–zirconium alloy showed no measurable attack, niobium crystals were found in the cold leg of the loop. This loop was operated for 5000 hr at a maximum temperature of 1400°F, with a temperature gradient of 400°F. The hot legs of the steel loops, which were operated at somewhat lower temperatures, exhibited general surface removal and a few large pits.

Other corrosion studies involving lead and tin alloys were reported at a recent symposium sponsored by the AEC. The dissolution kinetics of tantalum in liquid tin were investigated under well-defined hydrodynamic conditions produced by a rotating disk.[69] The velocity dependence of the maximum dissolution flux of tantalum under laminar flow conditions was determined at temperatures between 900 and 1100°C. Studies of the corrosion of refractory metals and their alloys by bismuth, tin, and lead at temperatures above 800°C were also reported.[70] Static tests with bismuth and tin were made on the following materials: molybdenum, niobium, tantalum, tungsten, molybdenum–30 wt.% tungsten, molybdenum–50 wt.% rhenium, niobium–1 wt.% zirconium, and niobium–10 wt.% tungsten–2.5 wt.% zirconium. Thermal convection loops fabricated from molybdenum–30 wt.% tungsten alloy and from tantalum were operated with bismuth–30 at.% sodium and lead–30 at.% sodium, respectively. The hot-leg temperature in these loops was 1050°C, and the cold-leg temperature was 700°C.

Miscellaneous

PROCESSES UTILIZING FUSED NITRATE SOLVENTS

Separations of fission products from irradiated UO_2 in molten nitrate salts were reported. When irradiated UO_2 was dissolved at 180°C in a nitrate melt containing NH_4NO_3 and the resulting melt was passed through a chromatographic column packed with activated alumina, the following order of elution was observed:[71] (Cs, Ba, Ru) → (U) → (La, Ce) → (Zr–Nb). The extent of uranium separation from the cesium–barium–ruthenium fraction, which was not adsorbed on the column, was dependent upon the NH_4NO_3 content of the melt. Complete separation of uranium from the rare-earth and zirconium–niobium fractions was possible.

Fission-product ruthenium was rapidly volatilized from irradiated UO_2 dissolved in $LiNO_3-KNO_3$ melts at temperatures of 260 to 280°C. Iodine was evolved from a similar melt containing NH_4NO_3. When a $LiNO_3-KNO_3$ melt containing dissolved UO_2 was heated to 350°C, an insoluble uranate precipitated. Nearly all the cesium, barium, strontium, and neodymium remained in the supernatant solution, but 35% of the lanthanum and 99% of the cerium coprecipitated with the uranate.

A pyrochemical "head-end" step for the separation of large amounts of molybdenum from uranium was reported.[72] Uranium dioxide dissolved in alkaline nitrate melts ($NaNO_3$, $NaNO_3-NaOH$, or $NaNO_3-Na_2CO_3$) formed insoluble uranates or diuranates at temperatures of 500 to 800°C, whereas molybdenum formed soluble sodium molybdates. The uranium compound, which was easily separated from the molten salt by filtration, contained less than 1% of the molybdenum. With appropriate temperatures and salt compositions, some removal of other fission-product elements can be achieved.

LIQUID-METAL CHEMISTRY

A compendium of the solubilities of various metals in liquid zinc has been issued.[73] The temperature dependence of the solubility is given, and the solid phase in equilibrium with the saturated solution is identified in most cases.

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Section

IV

Reactor Fuel Processing

Waste Disposal

By P. Fineman

Treatment of Low- and Intermediate-Level-Activity Wastes

Ion Exchange, Electrodeionization, and Electrodialysis

In the various countries associated with the European Nuclear Energy Agency, research and development work is being conducted on the treatment of radioactive contaminated liquid wastes by ion exchange, electrodeionization, and electrodialysis. Lopez-Menchero[1] has reviewed some of this work in a paper presented at a symposium on Practices in the Treatment of Low and Intermediate Level Radioactive Wastes held in Vienna on Dec. 6–10, 1965.

ION EXCHANGE

The sorption of various contaminants, such as cesium, strontium, rare earths, and cobalt, from low-level-activity wastes by naturally occurring and synthetic inorganic ion exchangers is being studied by research workers in the Netherlands, Italy, France, Belgium, Germany, and England.

In the Netherlands several selected Dutch clays and peats were examined for their ability to remove radioactive contaminants from contaminated surface waters. The following preliminary conclusions were indicated by the results: (1) River clay (1000 to 1200 ppm) efficiently removed low levels ($< 10^{-3}$ ppm) of cesium and yttrium; their sorption was practically unaffected by the presence of calcium and sodium ions. The sorption of cesium and yttrium decreased in the presence of 40 ppm potassium ion when low concentrations of clay were used; however, when larger amounts of clay were used, their sorption was not affected by potassium ion in the range of concentrations usually found in surface waters. In contrast, strontium and cobalt were not effectively removed by the river clay because the high calcium content in the surface water decreases their sorption. (2) Peat appeared very promising for strontium removal; it has a relatively high exchange capacity and excellent filtering properties. The exchange capacity of the peat for strontium was hardly affected by the monovalent-ion content of the surface water, whereas the capacity was very much determined by the calcium-ion content of the water.

In Italy several Italian volcanic materials (tuffs) were investigated for their ability to sorb cesium and strontium.[2,3] Volcanic materials representative of different types of zeolitic structure (analcitic, chabazitic, and phillipsitic) were tested using standard feed solutions traced with either ^{137}Cs or ^{89}Sr. Of the three materials tested, sorption capacities were highest for the chabazitic (1.87 meq/g) and the phillipsitic (1.74 meq/g) materials. Cesium and strontium distribution coefficients, K_d^M, (concentration of cesium or strontium in solid phase/concentration of cesium or strontium in liquid phase) for these two materials were obtained. The K_d^{Cs} for the phillipsitic material (60,000) was greater than for the chabazitic material (25,000). However, the K_d^{Cs} for the chabazitic material was increased to about 44,000 after it was subjected to heat-treatment at 400°C for 14 hr. The K_d^{Sr} for the chabazitic material (530) was greater than for the phillipsitic material (400). In further work with these two materials, the effects of *p*H and concentration of sodium and calcium ions on the K_d's for cesium and strontium were studied. The cesium and strontium K_d's for both materials increased when the *p*H was increased from 2.0 to 3.4 and did not change appreciably from the value at *p*H of 3.4 when the *p*H was increased further to 12. Increasing the sodium or calcium concentration (from 0.005*N* to 0.1*N*) in the feed solution reduced the cesium K_d for both materials, although they were still at relatively high values. The effect was more pronounced for sodium than for calcium.

In France and Belgium inorganic ion exchangers capable of being used with high-acid-content solutions are being developed.[1] Workers at St. Gobain Techniques Nouvelles (France) have prepared a ferrocyanide-based ion exchanger (glass-wool supported). Extremely high cesium decontamination factors have been shown for this ion-exchange material. Researchers at the Centre d'Étude de l'Énergie Nucléaire (Belgium) have prepared the following new synthetic mineral ion exchangers: ferrocyanide molybdate and ferrocyanide tungstate, which have a high

affinity for cesium,[4] and polyantimonic acid, which has a high selectivity for strontium.[1] Columnar tests of the ferrocyanide molybdate have shown that a maximum loading of 3.85 meq of cesium per gram of exchanger can be achieved. The loading capacity of the column was not affected at feed flow rates of 10 to 15 column volumes/hr; however, if high cesium decontamination factors (>10^4) are required, the flow rate should be reduced to 5 to 10 column volumes/hr. Because of the high affinity of the exchanger for cesium, quantitative elution is quite difficult, even with concentrated ammonium salts. A volatilization method was successfully developed in which the ferrocyanide molybdate is chlorinated. The reactions taking place are as follows: the molybdenum chlorides are volatilized below 200°C; the ferrocyanide decomposes at about 200°C and leaves CsCl and $FeCl_3$ in the residue; and, between 300 and 400°C, $FeCl_3$ volatilizes and leaves solid CsCl and some impurities. Studies were also conducted with the polyantimonic acid exchanger. Sorption kinetics for strontium were studied, and distribution coefficients of alkali and alkaline-earth and rare-earth elements were measured. The measurements showed the following: (1) strontium is sorbed by the exchanger at a rather low rate and (2) the distribution coefficients indicated that the alkaline earths are more strongly sorbed than the alkali elements except sodium and that the rare earths are intermediate between the two. Other work with the polyantimonic acid exchanger was concerned with recovering the strontium from the exchanger to which it is irreversibly fixed. The volatilization method, similar to that used for the ferrocyanide molybdate exchanger, has been successfully used. The polyantimonic acid is treated with hydrogen chloride at 270°C and forms volatile $SbCl_5$ and $SbCl_3$; thus only $SrCl_2$ and some impurities remain.

Workers at the Société d'Applications pour l'Industrie, a Belgian syndicate of engineering firms, have prepared a new series of mineral ion exchangers.[1] One of these exchangers, titanium phosphate, has exhibited a high loading capacity for cesium, even in concentrated acid (HNO_3) media.

In Germany, at the Technical University of Darmstadt, workers have developed inorganic ion exchangers consisting of highly insoluble ionic crystals on the surface of an inorganic matrix such as silica gel.[1] They have tested the following compounds in column runs: (1) barium sulfate, which has a very high selectivity for strontium and radium; (2) silver chloride, which has an extremely high selectivity for iodide ions; and (3) tungsten trioxide, which has shown a high selectivity for cesium. In other work these workers have synthesized another new series of inorganic ion exchangers. These are the insoluble metal phosphates and hexacyanoferrates of the following elements: zirconium, tungsten, molybdenum, titanium, vanadium, and aluminum. Studies of these ion exchangers have shown them to be stable in acid media, to have a very high selectivity for cesium, and to have medium to high saturation capacities.

In England, at the Imperial College (London), a group of researchers has investigated the irradiation degradation of commercially available cation and anion organic ion exchangers (polystyrene-based resins with sulfonic acid and quaternary ammonium functional groups).[1] Irradiation dose rates of 6 to 8×10^5 rads/hr have been used to achieve total doses up to 2×10^9 rads. Degradation of the resin structure occurs as a result of irradiation and leads to a loss in exchange capacity. Cation-exchange resins (Zeokarb-225 resin) were observed to be appreciably more stable to gamma irradiation than the anion-exchange resins tested. The exchange capacities of hydrogen- or sodium-form cation resins decreased from 4.4 to 2.8 meq/g for total doses of 1×10^9 and 1.4×10^9 rads, respectively. With the strong-base anion resins (hydroxide form), there is almost complete loss of exchange capacity at 10^9 rads. Nitrate forms of anion resins irradiated in 7 *M* HNO_3 underwent severe chemical and physical degradation, with evidence of complete destruction of the resin at a total dose of 8×10^8 rads.

ELECTRODEIONIZATION

The British have been conducting laboratory and pilot-plant studies of electrodeionization.[1] Laboratory work has been carried out with three-cell and five-cell units. In the five-cell unit, the two outer electrode cells were separated from the deionization cell by concentration cells. The deionization and concentration cells were filled with ion-exchange resins (Deacidite FF or Zeokarb-225; 14- to 25-mesh particles). The permselective membranes used in the construction of the two units were types TNO A-60 and C-60. The results of electrodeionization experiments have shown the following: (1) The concentration factors obtainable are limited by the permselectivity of the membrane, but factors of 100 or more have been obtained experimentally. (2) The proportions of anion and cation resins present in a mixed bed and their conductivity affect the ratio of anion removal to cation removal. (3) Mass transfer in electrodeionization cells is dependent on the distribution of anion–cation resin junctions within a bed and on the way in which these influence the transfer of ions from one particle to the next. (4) Mass transfer from solution to resin is film-diffusion controlled at low concentrations and is therefore influenced by solution flow rate. (5) Concentration polarization at the resin–solution interface unfavorably affects mass transfer at low concentrations. This leads to a limited removal rate that cannot be improved by the use of high current densities.

The British have also placed two electrodeionization pilot plants in operation. The first plant has a capacity of 1000 liters/hr and consists of an unfilled electrodialysis cell followed by three resin-filled cells. The second plant has a throughput of 2000

liters/hr and comprises two multicompartment resin-filled stacks in series. The membrane area of this plant is one-half that of the 1000 liter/hr plant. The two pilot-plant units use mixed-bed ion exchangers, the 2000 liter/hr unit being completely filled with the mixed-bed resins. Although there is a large difference in power consumption between the two plants, operation of the larger throughput plant might be cheaper since it uses only one-half the membrane area, and the membranes represent the most expensive maintenance item, even if a 5-year life is assumed.

ELECTRODIALYSIS

Workers at the Centre d'Étude de l'Énergie Nucléaire (Belgium) are studying the application of electrodialysis to desalting the cesium-containing eluate from zirconium phosphate or ferrocyanide molybdate ion exchangers.[1] Laboratory experiments were conducted on the desalting of ammonium nitrate solutions. Treatment of $2M$ NH_4NO_3 solutions containing 5 g of cesium per liter resulted in 99% removal of the salt; of the remaining 1% of the salt, 0.8% was found in the catholyte, and 0.2% had diffused into the anolyte.

Incorporation in Asphalt

Oak Ridge National Laboratory (ORNL) is continuing work on the use of asphalt as a medium into which intermediate-level-activity wastes (ILW), after concentration in an evaporator, are incorporated in asphalt.[5,6] (Plants for incorporating ILW in asphalt have been constructed in Belgium and France.[6,7]) In the process the ILW concentrate (up to 60 wt.% salts) is introduced by stirring (100 to 300 rpm) into an emulsified asphalt that contains about 35 wt.% water; the asphalt mixture is heated to about 160°C to evaporate the water, and the product mixture is then poured into a container.[6] The process has a number of desirable features, which include the following: (1) use of emulsified asphalt, which flows readily at room temperature; (2) evaporation at low temperature, which minimizes activity entrainment and asphalt degradation; (3) low mixing rates, which provide adequate mixing and keep the heated surfaces of the evaporator clean; (4) operation in batch or continuous manner; and (5) incorporation of both soluble and insoluble materials with equal effectiveness.

Recent ORNL work has been concerned with the safety characteristics of asphalt products containing nitrate salts.[6] (The fixation of inert solids in asphalt does not appear to present any additional hazard to that normally present when processing, storing, or shipping an organic material with a high flash point.) Tests have been carried out with irradiated asphalt samples (1 to 2 g) containing 35 wt.% nitrate (total salts, 60 wt.%) to determine their flash point and ability to sustain combustion in the absence of external oxygen. A flash point of about 280°C was found for these irradiated samples, which is slightly lower (~50°C) than that noted for unirradiated asphalts. A flame was easily extinguished when the air was replaced by nitrogen, even though the solid-phase temperature was in the range of 400 to 500°C. Other safety tests are to be conducted by a commercial laboratory, under a subcontract to ORNL, on asphalt products containing various amounts of added nitrate salts. These tests will include those of stability, including drop weight, autoignition, shock sensitivity, and flame propagation. Large-scale fire tests involving 30-gal drums of asphalt products are also planned.

Conversion of High-Level-Activity Wastes to Solids

Some of the papers presented at the USAEC-sponsored symposium* on the solidification and long-term storage of high-level-activity wastes were summarized in the preceding issue of *Reactor Fuel Processing*.[10] Additional papers from this symposium have become available, and these are summarized below.[11]

Pot and Spray Calcination Processes

FRENCH POT VITRIFICATION PROCESS

At the Centre d'Études Nucléaires, Fontenay-aux-Roses, France, a pot process is being developed for the vitrification of the concentrated fission-product waste solutions produced in the processing of natural-uranium fuel from the Marcoule, France, production reactors.[11] The process consists of the following steps: (1) evaporating the waste solution plus added glass formers in an inductively heated Inconel calcination pot until it is 75% full, (2) gradually raising the temperature to 1150°C in order to calcine the nitrates present and to melt the glassy solid formed, and (3) draining the molten glass from the calcination pot into a storage vessel. The pot is expected to be used 30 times before being replaced. At times the molten glass will not be drained from the pot, and the pot itself will serve as the storage container. The process off-gases are treated as follows. They pass through a heated (200°C) line to a ruthenium filter, which is a bed of granular oxide and is maintained at 500°C. They then pass through a vertical condenser, after which the noncondensable gases go to a second ruthenium filter, which is identical to the first. From this filter the gases pass through three adsorption towers (with circulating sodium hydroxide) and finally through an absolute filter.

Successful nonradioactive and low-level-activity engineering-scale tests of the process have been

*Publication of the entire proceedings of the symposium is planned. Summary accounts of this symposium have been presented in two journal articles.[8,9]

carried out with synthetic Marcoule fission-product waste solutions. Silicate-glass formers were used in these tests. The inactive runs demonstrated the following: feed flow rates of 15 to 20 liters/hr, volume reductions of up to 10, and molten-glass flow rates of up to 80 kg/hr. One of the calcination pots used for 20 vitrification cycles showed practically no corrosion. The radioactive runs showed that ruthenium volatility from the melt amounted to about 20% and that the removal efficiency of the first ruthenium filter was low (~50%). It is believed that increasing the size of this filter to increase the off-gas retention time will improve the ruthenium-removal efficiency. Also, it was successfully shown that the iron oxide granules (saturated with ruthenium) from the ruthenium filters could be formed into a glass for disposal purposes. Only a small amount of ruthenium was volatilized in this operation. Construction at Marcoule of a pilot plant capable of handling highly radioactive solutions is planned.[9]

ORNL POT PROCESSES

Three pot processes (Fig. IV-1) for the fixation of high-level-activity wastes are being developed at ORNL.[12] All three processes produced solidified waste in a cylindrical vessel (pot) suitable for permanent storage. If the solid product is to be a calcine (pot calciner or Potcal process), the pot is operated at a constant liquid level. Up to about 95% of the pot volume can be filled with solids. Additives to the waste are required only when necessary to prevent volatilization of some component (e.g., SO_3, cesium, or rubidium). If a glass or a ceramic solid is to be the final product [rising-level (RL) potglass process], the necessary additives are added to the waste either in the pot or in the feed line. The liquid level is kept quite low in the pot until the first calcine has formed and then melted. The feed rate is then increased until the rate of melting calcine just equals the rate at which fresh calcine is formed. Thus there is present a constantly rising pool of melt covered by a relatively thin layer of calcine, which is in turn topped by a layer of liquid waste.[13] In the continuous (CON) potglass process, the waste solutions with additives are fed to a continuous melter from which the melt is discharged to the storage pot. The storage pot can be identical in size and shape to those used in the Potcal and RL potglass processes but would be simpler in construction and should therefore be less expensive. The CON potglass process is attractive from an operating standpoint since operation is truly steady state as opposed to semicontinuous operation in both Potcal and RL potglass processes, and the aqueous feed is converted directly into glass.

Clark and associates,[11] ORNL, summarized the laboratory-scale investigations carried out on the development of these processes. A wide variety of simulated waste solutions was tested; these included wastes generated by the processing of aluminum-clad uranium fuels (Purex process), stainless-steel-constituted fuels (Darex process), and enriched-uranium – aluminum alloy fuels (TBP-25 process). Melt development was principally based on the use of phosphate as the main matrix material because melt temperatures can generally be kept low (850 to 900°C), its additives are water- or acid-soluble, and homogeneous melts are possible with high-sulfate-content wastes. The results of these tests were as follows:

1. The Potcal process readily handled all the waste types studied. The RL potglass process was success-

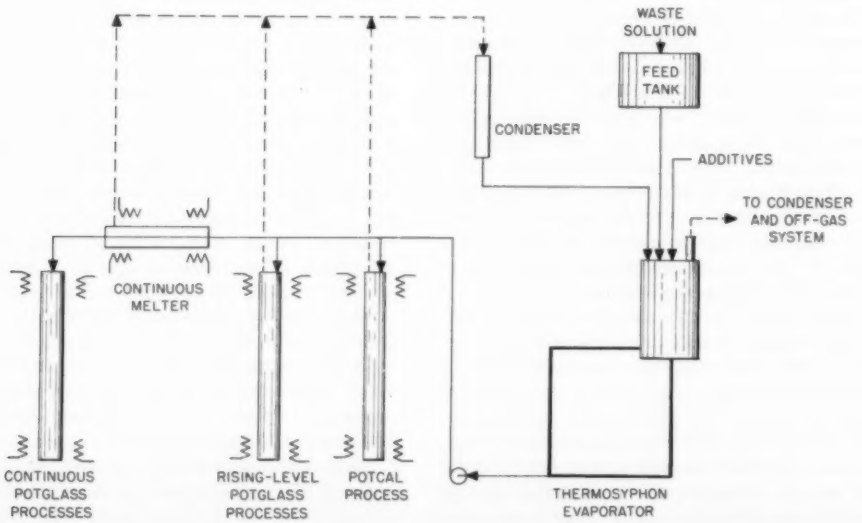

Fig. IV-1 Schematic flow sheet for the ORNL pot processes for fixation of high-level-activity radioactive waste.[11]

fully demonstrated with TBP-25 wastes and Purex wastes free of sulfate or containing sulfate. In the two processes, corrosion of the fixation pot (stainless steel) was kept to a satisfactorily low level by keeping fixation temperatures below 900°C and by adding reductants to wastes high in iron and chromium. Operation of the CON potglass process was simpler than the other two processes. However, low-melting and noncorrosive melts are required to prolong the operating life of the continuous melter.

2. Volatilization of cesium, rubidium, ruthenium, and sulfate was effectively controlled in all processes. Replacement of mercury in a waste by copper or aluminum was more practical than trapping it from the off-gas.[14]

Suddath and associates,[11] ORNL, described the engineering development of the three pot processes being evaluated at ORNL. They covered the following: (1) the engineering-scale tests with nonradioactive simulated Purex, TBP-25, and Darex wastes which provided information needed for the design of the pilot plant constructed at Pacific Northwest Laboratory (PNL) for testing selected solidification processes with highly radioactive wastes; and (2) equipment development.

BROOKHAVEN PHOSPHATE-GLASS PROCESS

In a process developed at Brookhaven National Laboratory (BNL), a phosphate glass is produced directly and continuously from an aqueous process waste without a separate intermediate drying step.[15] For a wide range of waste compositions, phosphoric acid is the only necessary additive, although metal ions may be added to improve the glass characteristics. The steps in the process consist in admixing phosphoric acid with the waste, then evaporating the resulting solution at 140 to 160°C to reduce its volume, and finally heating the concentrated solution to 1200°C to form the glass. This process has been tested at BNL with simulated solutions[16] and at PNL in small-scale in-cell equipment with actual high-level-activity wastes.[15] (The experiments conducted in the in-cell equipment are described in another symposium paper by Upson, PNL, and Weth, BNL.[11]) Plans are under way to carry out tests of this process in the pilot-plant facility at PNL.[17] Information needed for the design of the equipment and the process is being developed jointly by BNL and PNL. The prototype evaporator to be used in the demonstration of the Brookhaven process is of a new design (prepared at PNL). It was decided that, in addition to the prototype evaporator that is being built at PNL, a similar evaporator would be fabricated at BNL and tested there. (The lower portion of the BNL-fabricated evaporator is shown in Fig. IV-2.*) The operation of the

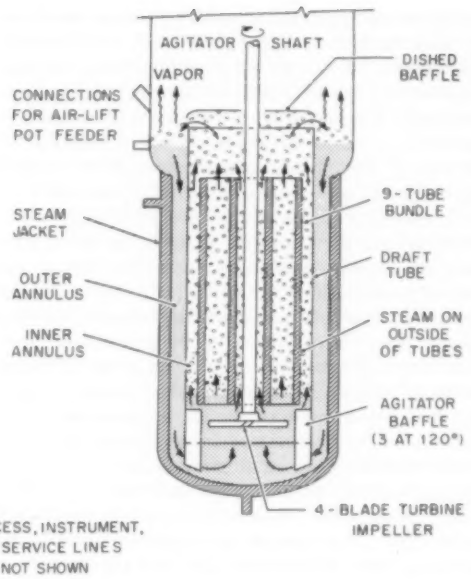

Fig. IV-2 Schematic details in lower half of BNL-fabricated evaporator.[11]

evaporator is as follows: boiling action induces a positive flow of solution upward through the tubes and in the annulus (inner) between the tube bundle and the draft tube The turbine agitator serves to improve circulation during operation and minimizes settling under conditions of nonboiling and low circulation rate. Agitator baffles ensure the upward flow of solution through the tubes.

Strickland and associates,[11] BNL, reported on the preliminary evaporator tests. The objectives of these tests were to obtain operating experience, performance data, and process information. Simulated Purex type wastes were used as feed solutions in the tests. From the operating experience obtained in the tests, a procedure for the satisfactory operation of the evaporator was established. Foaming was found not to be a serious problem. The data indicated that continued testing should be at an operating temperature of about 130°C. It was observed that high initial heating rates caused scaling and consequent reduction in performance; further work is therefore needed to determine an optimum initial temperature drop across the tubes in the tube bundle and heat-up time. The scale was removed with a cleaning solution containing nitric acid and phosphoric acid. It was recommended that agitator baffles be added to the prototype evaporator being fabricated at PNL.

The condensate produced in the glass-forming step of this process is a secondary high-level-activity waste that will contain appreciable amounts of sulfuric and nitric acids and a small amount of phosphoric acid.[17] Mercer and associates,[11] PNL, presented

*The PNL design of the prototype evaporator did not originally include agitator baffles. Baffles were added to the BNL-fabricated evaporator after shakedown runs had been completed; they ensure upflow through the tubes.

a survey of methods for the treatment and disposal of this condensate. They discussed two general approaches. One approach consists in converting the condensate or the sulfate contained therein to solids that will retain all or a portion of the fission products. The other approach involves separating the sulfate from the fission products, which would then be recycled to the phosphate-glass process.

In the first approach the following methods were considered: (1) precipitation; (2) formation of plaster-like materials, glasses, or melts; and (3) incorporation into mortar or asphalt. Since precipitated solids, plasters, and cement mortars are subject to relatively high leach rates, these materials would be limited to wastes having low fission-product concentrations. Although asphalt-waste mixes are reported to have relatively low leach rates, radiation stability may be a problem at high fission-product concentrations. Sulfate glasses or melts exhibit low solubility; however, the preparation cost would be prohibitive.

In the second approach the following methods were examined: (1) ion-exchange separation of sulfate, (2) scavenging of fission products, and (3) crystallization of sodium sulfate. Ion exchange does not appear attractive because of the high acid concentration of the condensate. Scavenging with a mixture of hydrous manganese dioxide and ferric oxide offers a fine means of removing fission products from the condensate since a substantial portion of the fission products can be recycled to the phosphate-glass process. Sodium sulfate crystallization experiments showed that more than 90% of the fission products can be separated from the bulk of the sodium sulfate crystals. (Ninety percent of the sodium sulfate is crystallized.) A water rinse at 0°C increased the fission-product separation to 98 to 99%.

Mercer and associates believe that, at high fission-product concentrations, separation of the fission products and their recycle to the phosphate-glass process is the most promising approach.[18] The residual sulfate may then be disposed of as an intermediate-level-activity waste by methods such as in-tank solidification[19] or incorporation in asphalt.

RADIANT-SPRAY CALCINER AND MELTER

A spray-solidification process for high-level-activity wastes is being developed at PNL.[20] It is one of the three waste-treatment processes scheduled for testing in the demonstration program at PNL. In spray solidification, liquid waste is spray-fed into the top of a heated column. The spray droplets are progressively dried and calcined to a powder as they fall down the column. The powder falls directly into a melter, where the powder is dissolved in the molten waste at 700 to 1200°C. The molten waste then flows into the final storage vessel (maintained at or near the melting point of the waste) through an overflow weir or through a freeze valve. The storage vessel is then cooled and sealed for storage. The process off-gas is passed through porous metal filters. The filters are periodically cleaned of filter cake or powder by pulses of high-pressure steam directed backward through the filters. The dislodged powder falls into the melter. Engineering-development studies with nonradioactive simulated wastes and small-scale pilot-plant studies with actual plant-level wastes of the spray-solidification process are described in two reports. The first report by Kaser and Moore,[11] PNL, summarizes the extensive nonradioactive work carried out with plant-scale equipment. These experimental studies provided data for designing the equipment to be used in the waste-solidification demonstration program. The second report[11] (R. L. Moore, PNL) discusses the plant-level-activity runs that were undertaken. These runs demonstrated the feasibility of spray calcination of plant-level-activity wastes and showed that the radioactive off-gas could be readily decontaminated to safe discharge levels. It was also shown that the spray calciner was capable of being remotely operated with a variety of feeds, including alkaline and acidic wastes, thick slurries and true solutions, and feeds containing a variety of glass-forming additives. A wide variability in the composition of plant-level-activity wastes was encountered; this implied that any solidification process based on wastes of a narrow composition range would experience operating difficulties.

Engineering Demonstration of Solidification Processes

At PNL a multipurpose facility, known as the Waste Solidification Engineering Prototypes (WSEP), has been constructed to demonstrate the technical, economic, and safety aspects of three selected solidification processes: the ORNL pot calcination and rising-level glass processes, the BNL phosphate-glass process, and the PNL spray-solidification process.[17] Cooley and Platt,[11] PNL, outlined and discussed the experimental program planned for the WSEP. They presented the following as the overall objectives of this program:

1. To define liquid-waste characteristics that are suitable for solidification.
2. To produce fully radioactive solid products ranging from calcines to glasses for study.
3. To evaluate the quality and stability of the solid product as affected by the process used, the geometry of the product, and the interim and final storage environment.
4. To demonstrate the permanent sealing of containers necessary to maintain long-term integrity.
5. To obtain technology necessary for the design and operation of a solidification plant.
6. To confirm and establish the practical and safe manner in which waste can be solidified and stored.
7. To characterize the low-level-activity and intermediate-level-activity wastes from the solidifica-

tion processes and their treatment for disposal or recycle.

The major portion of the experimental program will be demonstrated with two principal types of high-acid (5*M*) Purex waste. One type is a first-cycle Purex waste (PW-1) that does not contain sulfate ion, but does contain added iron from the dissolvable container used to transport chopped fuel. The other Purex waste is a combined first- and second-cycle waste that does contain iron and sulfate ions from the ferrous sulfamate reductant, but does not include iron from the dissolvable container. The fission-product distribution in the two wastes is equivalent to a burnup of 20,000 Mwd per metric ton of uranium. The demonstration of other waste types will be limited; these include TBP-25 and Darex process wastes, zirconium-bearing wastes, and wastes from the processing of thorium and other advanced reactor fuels.

Extensive information on the mechanical design features of WSEP equipment was presented by Schneider and Kelly,[11] PNL. Rey and associates,[11] PNL, have reviewed the design verification testing conducted with simulated wastes in the WSEP. Equipment components and the chemical flow sheets for pot calcination, rising-level glass process, and continuous spray solidification were successfully tested. During the course of the testing, changes in equipment design and new developments in flow sheet that were made were incorporated in the tests. On the basis of these tests, the authors concluded that the pot and spray-solidification processes were ready for demonstration with radioactive wastes.

Current Work on Solidification Processes

RISING-LEVEL POTGLASS PROCESS

In recent work at ORNL, the rising-level (RL) potglass process was tested in two engineering-scale experiments with simulated Purex-based wastes (PW-1) containing nonradioactive fission-product elements.[21,22] Lithium and sodium phosphates were added as glass formers, and sodium phosphite was added as a reductant to decrease corrosion of the pot (type 304LC stainless steel). The operating temperature of the pot was maintained at 900°C. In the first experiment, which was completed in 67 hr, an 8-in.-diameter by 96-in.-long pot was used; the PW-1 waste, the glass formers, and sodium phosphite were combined in the feed tank and then fed directly to the pot as in previous experiments. Although a precipitate formed in the feed tank, which made it difficult to control the flow rate of the resultant slurry to the pot, the test was completed, and a satisfactorily dense glassy product was formed. Corrosion of the pot was negligible, less than 5 mils. In the second experiment, which was completed in 100 hr, a 12-in.-diameter by 72-in.-long pot was used. The glass formers and the sodium phosphite were first combined and then introduced as a separate stream to the waste feed line to the pot; the two streams were to be fed in a ratio of additives to waste of 0.34 to 1. Occasional plugging of the additives and waste feed lines occurred during the course of the run. The lines were sparged with high-pressure water to remove the plugs. Operational difficulties (plugging) with the liquid-level probe in the additives feed tank caused the ratio of additives to waste stream to vary from 4 to 0. However, it is believed that the variations in flow rate can be controlled and prevented by suitable equipment modification. Otherwise the feeding operation proceeded satisfactorily in the absence of significant amounts of solid. Consequently the use of separate streams is recommended for this process. The large variation in the ratio of additives to waste probably did have an effect on the uniformity of the composition of the final glass product. This variation in product composition may have contributed to the high corrosion (up to 239 mils) observed in the bottom zones of the pot; the amount of corrosion decreased to very near zero at the top zone.

In supporting laboratory studies at ORNL, satisfactory phosphate-melt compositions were developed for fixation of PW-1 and PW-2 wastes in glassy solids.[22] Lead silicate-melt compositions were also developed for PW-2 wastes. The lead silicate melts were more homogeneous in appearance, had lower softening and operating temperatures, and produced higher volume reductions than the phosphate melts.

Laboratory-scale experiments of the RL potglass process were performed using simulated PW-1 and PW-2 wastes containing fission-product elements equivalent to a burnup of 20,000 Mwd per metric ton of uranium. In order to carry out fixation of PW-1 wastes with phosphate-glass formers at reasonable rates, slightly higher operating temperatures (900 to 950°C) were required than the 900°C maximum that is desirable for a stainless-steel pot. At about 950°C corrosion was fairly severe. However, substitution of 0.1*M* hypophosphite for an equivalent amount of phosphate in the melt decreased the corrosion markedly; the optimum amount of hypophosphite has not yet been determined. Volume reductions (volume of liquid waste/volume of solid product) varied from 5.7 to 9, which corresponded to 11.1 to 17.5 gal of solid product per metric ton of uranium processed. Ruthenium volatilization varied from 24 to 53% of the charge; the lower value occurred when a maximum amount of hypophosphite was present. Molybdenum volatilization varied from 0.4 to 1% of the charge.

For PW-2 wastes, fixation with phosphate-glass formers was successfully accomplished at lower operating temperatures (800 to 850°C). Sulfate volatilization amounted to 11 to 15% of the sulfate present. (Previous work had shown that sulfate volatilization can be made almost negligible if the equivalents of alkali and alkaline-earth cations present in the waste are slightly greater than the equiv-

alents of nonvolatile anions.) Volume reductions of 7 were achieved, which is equivalent to about 14.3 gal of solid product per metric ton of uranium processed.

FLUID-BED CALCINATION

The initial operation of the Waste Calcining Facility (WCF) at the Idaho Chemical Processing Plant (ICPP) was completed in October 1964 (Refs. 23 and 24). In the WCF, plant-level-activity aqueous wastes from the processing of aluminum–uranium fuels were converted to granular solids in a fluid-bed calciner (Fig. IV-3). In the 312 days that the WCF was operated, about 512,000 gal of wastes was converted to 7500 cu ft of solids,* which weighed some 412,000 lb (Ref. 24). Process performance was excellent, and decontamination of the calciner off-gas was very satisfactory. No corrosion problems of major importance were observed on any of the WCF equipment items.

After scheduled repairs and modifications to the WCF were completed, operation of the WCF with a highly radioactive aluminum nitrate–nitric acid waste was resumed on Apr. 1, 1966 (Ref. 27). In the first month of operation, about 40,000 gal of waste was calcined, and operation of the WCF, in general, has been very satisfactory. The mass median particle size of solids in the calciner bed has been maintained in the desired size range, 0.55 to 0.65 mm. The bulk density of the bed has averaged about 1.1 g/cm^3, and the carry-over of solids to the scrubbing system has averaged about 8.7 lb/hr. The calcined solids are being stored in the seven recently completed bins (see Fig. IV-4).[28] (A solids-flow diverter valve is being used for directing the flow of calcined solids to two of the seven new bins. Petrie and Cooper, ICPP, describe this diverter valve, its principle of operation, and its testing in a recently issued report.[29])

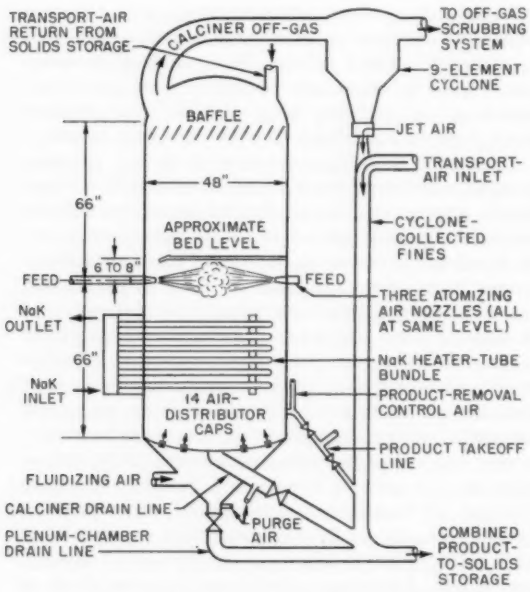

Fig. IV-3 Fluid-bed calciner vessel and auxiliary equipment in Waste Calcining Facility, National Reactor Testing Station, Idaho.[24]

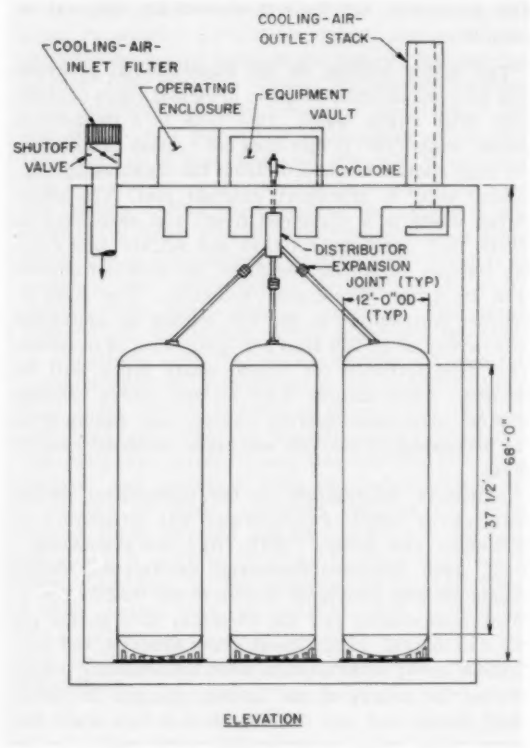

Fig. IV-4 Elevation view of new storage bins at Waste Calcining Facility.[24]

Decontamination of off-gas from the calciner has also been satisfactory; release rates of ^{90}Sr and total ruthenium (^{103}Ru and ^{106}Ru) to the atmosphere has averaged less than 0.01% and less than 2%, respectively, of that which would cause a ground-level concentration equal to the permissible occupational exposure[30] as listed in the Radioactivity Concentration Guide.

*Work on the conversion of calcined solids to a glass form is being conducted at the ICPP. The preparation of alumina–phosphate glasses from plant-level-activity calcined alumina produced in the WCF and leach-rate data from testing samples of these glasses were reported in the Spring 1966 issue of *Reactor Fuel Processing*.[25] The details of the glass preparation and leaching studies are described in a report by Paige, ICPP.[26]

Mathematical Model for Fluid-Bed Calciners

Fluidized-bed processes involve particles that are in intimate contact with an upward flowing stream of fluid, usually a gas. Depending upon the process, these particles may grow or disintegrate, enter or leave the system, absorb or reject heat, transfer heat from one part of the system to another, provide surface area for catalytically induced reactions, or react with the flowing stream of fluid. Many of these phenomena occur together in a complex manner.

Grimmett,[31] ICPP, has proposed a mathematical model that describes the particle dynamics in fluidized-bed processes. This model includes the important factors of particle growth, particle attrition, elutriation of particles from the surface of the bed, and the addition of seed particles to the bed. Mathematical equations are presented describing both the steady-state and unsteady-state particle-size distribution in the bed. Digital-computer solutions of the unsteady-state model are presented to demonstrate its applicability to actual fluidized-bed processes, and the computer code for solving the unsteady-state equation written for an IBM-7040 computer is also presented.

Simulated calciner runs were compared with actual calciner runs made in 3-in.-diameter, 12-in.-diameter, and 2-ft-square calciners. Generally, good agreement between the simulated and the actual particle-size distribution of the beds was obtained in each case, even though there were striking differences between the sizes and operating conditions for the three calciners. On the basis of the simulation of the actual calciner runs studied, Grimmett believes that the mathematical model, with appropriate modifications, can be applied to a wide range of operating conditions and sizes of fluidized-bed calciners.

Final Disposal Methods

In-Tank Solidification

As part of the Hanford waste-management program, existing underground tanks will be utilized for permanent storage of intermediate-level-activity plant wastes that have been concentrated to a solid cake by in-tank evaporation.[32] Shefcik,[33] Isochem, Inc., Hanford, described the 10 months' operation of the first in-tank solidification unit; it was used in a 750,000-gal tank. The wastes were evaporated (additional wastes were also added during this step) within the tank by sparging with heated air (1200°F). The air sparger also served as an air-lift circulator. The moisture-laden air was treated; it was drawn from the tank through a deentrainer, a filter, a condenser, and finally exhausted to the atmosphere.

Some 1,500,000 gal of highly alkaline wastes were evaporated in this period. Wastes were reduced in volume by a factor of more than 3. However, more wastes will have to be evaporated in this tank before the solidification aspect of the process can be demonstrated on a full scale. No difficulties are anticipated, however, since solidification has been repeatedly demonstrated in the laboratory and pilot plant with simulated and actual wastes. (The waste solidifies on cooling after it has been reduced in volume to its terminal concentration; most plant wastes were usually concentrated by a factor of 4 to 6). The circulator for introducing the heated air into the waste has proved to be adequate. Residual activity in the treated off-gas has been low; decontamination factors of greater than 10^4 were routinely obtained. Although glass-fiber filters have proved satisfactory in treating acidic or neutral vapors, they became grossly deteriorated from the alkaline particles entrained in the vapors. (Work on deentrainment is in progress.)

Two additional in-tank solidification units are being built. These units will employ electric immersion heaters, which are placed within the air-lift circulators.

Calcined-Solids Storage in Salt Mines

The utilization of salt mines for the storage of high-level-activity solids is being demonstrated in the Carey Salt Company mine in Lyons, Kans.[34–36] The objectives of the demonstration are: (1) confirmation of feasibility and safety of disposal in salt mines; (2) demonstration of required waste-handling equipment and techniques; (3) determination of the stability of salt under the influence of heat and radiation; and (4) collection of information on creep and plastic flow of salt, which is needed for the design of an actual disposal facility. Fourteen irradiated fuel assemblies from the Engineering Test Reactor at the National Reactor Testing Station (NRTS), Idaho, serve as a source of radiation in lieu of actual solidified wastes. In November 1965 the assemblies, contained in seven cans, were placed in an array of holes in the mine floor.[37,38] During the course of the 2-year test, four sets of assemblies will be used to achieve a peak dose to the salt of about 8×10^8 rads, and the temperature of the adjacent salt will be raised to 200°C with auxiliary electric heaters. A second array will be installed in less pure salt (i.e., salt interbedded with shale) at the end of the first 6 months; this second array will use the fuel assemblies that are now in the main array. A third array, consisting only of heaters, is being operated as a control to determine those effects due solely to heat. In addition to the radioactive and control arrays, a rib pillar will be heated by electric heaters at its base to produce additional information on salt flow characteristics at elevated temperatures. Operation of the demonstration is proceeding routinely.

The first 50 days of operation have not revealed any significant effect of radiation on salt flow or stability.[38,39] Thermal expansion of the floor and increased transverse expansion rates in the pillars

adjacent to the array rooms have been about as expected. The acceleration of movement in the ceiling has exceeded that which was anticipated due to thermal effects in the floor; however, the magnitude of the movement is such that no trouble is expected from this source during the operation of the demonstration. Even in an actual operation, movements of this magnitude (or even greater) should not cause trouble during the time when a room is still being filled with waste. After the room is filled, it is anticipated that it will be backfilled with crushed salt. The increased roof movement does indicate, however, that an extra margin of stability must be allowed in the initial design of the disposal facility.

Fission-Product Recovery

Ion-Exchange Process for Cesium Recovery

Smit and Jacobs[40] describe an ion-exchange process for the large-scale recovery of cesium from acid fission-product wastes. The process is based on the selective adsorption on columns of the crystalline inorganic ion exchanger, ammonium 12-molybdophosphate (AMP). The useful capacity of AMP for cesium varies from 0.6 to 0.7 meq/g, depending upon the composition of the cesium-bearing solution. The process also does not require prior neutralization of the feed solution and is directly applicable to waste solutions of virtually any composition, provided they have a *p*H that is less than 5. The use of specially prepared, coarse-grade AMP allows suitably high flow rates. The process steps are as follows: (1) the cesium-bearing waste is passed through the column of AMP for adsorption of the cesium; (2) impurities are washed with dilute nitric acid; (3) the cesium is eluted with hot concentrated ammonium nitrate solution; (4) a chloride-catalyzed reaction is used to decompose the ammonium nitrate in nitric acid solution; and, finally, (5) the resulting solution is evaporated to recover the final cesium product (a mixture of CsCl and $CsNO_3$). Smit and Jacobs state that the principal advantages of the process are its simplicity, small size of equipment (relatively shallow beds of AMP are needed), small quantities of active waste produced, and its applicability to virtually any nonalkaline waste, including wastes of very high acid or salt content.

Other Literature

Advances in the technology of waste treatment and disposal and highlights of recent waste-management experience in the United States and abroad are presented in a review article by Belter, USAEC, and Pearce, PNL.[41] Included in this article is information on the following: management and treatment of radioactive liquid wastes from uranium mines and mills, power reactors, and fuel-reprocessing plants; handling of gaseous wastes from fuel-reprocessing operations; storage of liquid wastes in tanks and underground tunnels; storage of solid wastes from calcination and fixation of high-level-activity wastes; underground and sea disposal of packaged solid wastes having low-hazard potential; environmental studies; and, engineering, economic, and safety evaluation studies in connection with waste-management operations in a future nuclear power economy.

The feasibility of using solar energy for the evaporation of radioactive wastes was studied at the "Democritus" Nuclear Research Center, Athens, Greece.[42,43] A solar evaporator was designed, built, and then operated in the open for about 3 months (September to November 1965). The test solutions consisted of tap water containing added sodium chloride (5%) and radioactive bromine (^{82}Br; $t_{1/2}$ = 36 hr). The evaporative capacity of the solar evaporator was determined to be about 20 liters/8 hr when the maximum temperature of the evaporated liquid was about 50°C. The test results showed that solar evaporation of radioactive liquids in open air is possible without the danger of contaminating the environment.

At Chalk River, Canada, an incinerator plant (Fig. IV-5) has been operated experimentally to dispose of low-level-activity (up to 200 mr/hr on contact) combustible wastes.[44] The incinerator has a burning capacity of 500 to 550 lb per hour of waste and is capable of volume reductions of 96%. Combustion gases (flue gases) are cooled with ambient air before being decontaminated by filtration through glass-cloth bags in a baghouse dust collector. High-efficiency filters were provided but were not needed. On the basis of burning 150 tons of waste per year, an operating and amortization cost of 9.5 cents/lb has been calculated. Modifications and simplifications recommended for future incinerator plants will appreciably reduce this cost.

As part of the waste-management program at Hanford, ^{137}Cs and ^{90}Sr are among the various fission products that will be separated from the currently generated and stored plant wastes.[45–47] The separated cesium and strontium will be packaged in high-integrity containers and sent either to waste management or to the Fission Product Conversion and Encapsulation Plant, which is to be built by Isochem, Inc., by 1968 (Ref. 48). The packaging operation is as follows: the fission products are adsorbed on a bed of aluminosilicate zeolite in a stainless-steel container; the loaded zeolite is dehydrated by passing dry heated air through the bed; the container is purged with helium to increase the thermal conductivity of the zeolite; the container is then cooled and sealed (by welding). The container design permits the ready recovery of the fission products by their elution from the zeolite bed with $2M$ NH_4NO_3 (cesium) and $1M$ HNO_3 (strontium). Plans have been proposed to store the sealed containers underwater in an existing facility until needed.[49]

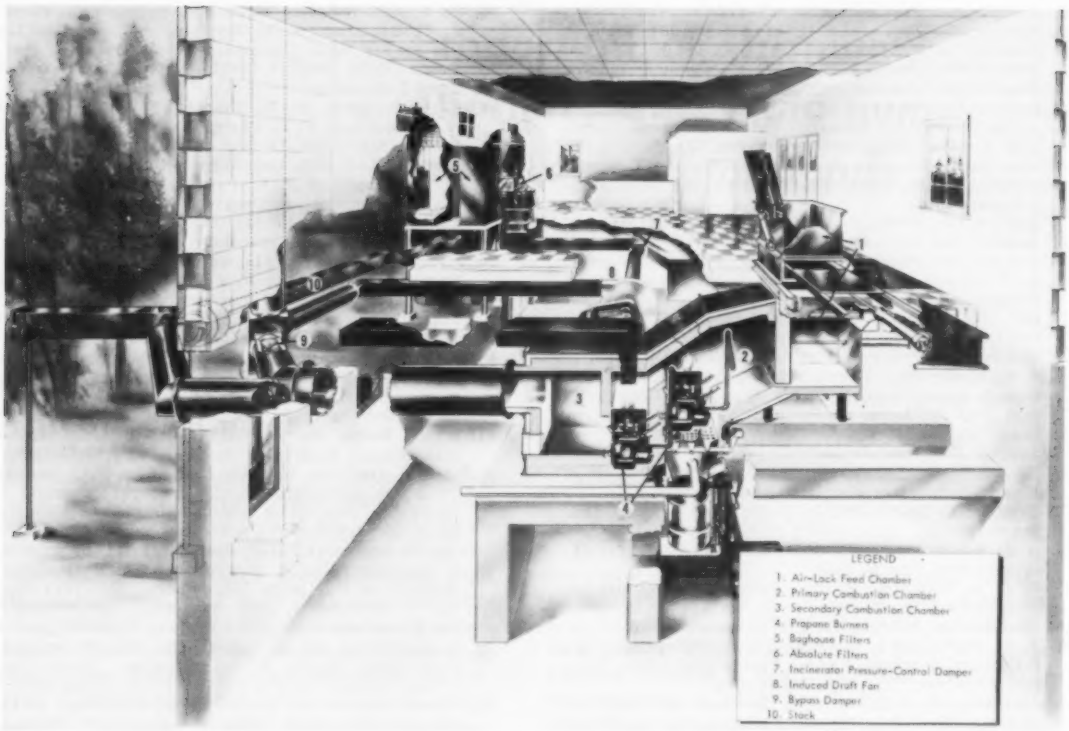

Fig. IV-5 Active-waste incinerator plant at Chalk River.[44]

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, and Plutonium and Their Compounds

By J. J. Barghusen

Production of Uranium Compounds by Hydrometallurgical Techniques

Uranium concentrates may be prepared by dilute aqueous leaching of the ore with ammonium carbonate solutions. Leaching at 25°C or at 100°C under an air pressure of 100 psi was effective in dissolving 90% of the uranium from certain ores to produce solutions containing 2 to 3 g of U_3O_8 per liter.[1] The leaching rate of ores containing phosphate was significantly higher than other varieties of ores. In certain cases, leaching of ores resulted in the formation of supersaturated solutions of uranium; it is suggested that an acceptable grade of uranium concentrate could be produced by crystallization of ammonium uranyl carbonate from such solutions.

Uranium was recovered from carbonate leach liquors containing 2 g of U_3O_8 per liter by removal of ammonia from the solution by steam stripping. When phosphate was present in the solution, uranium was precipitated as hydrogen autunite $[H_2(UO_2)_2(PO_4)_2 \cdot 8H_2O]$. In the absence of phosphate, uranium was precipitated as hydrated uranium trioxide ($UO_3 \cdot 2H_2O$). Over 99% of the uranium was recovered in the precipitate after 6 hr of steam stripping. The major impurities appearing in the uranium precipitate were V_2O_5, ZrO_2, SiO_2, Al_2O_3, TiO_2, CuO, and MgO. Exploratory tests were also performed to evaluate an alternative method for the recovery of uranium from ammonium uranyl carbonate solutions based on the catalytic reduction of uranium by hydrogen gas at 150°C and a pressure of 500 psi.

Kinoshita[2] has investigated a process for the recovery of uranium from ores based on leaching of the ore with Na_2CO_3 or $NaHCO_3$ solutions, solvent extraction of the uranium from the leach liquor, and precipitation of uranium as a double fluoride salt. The preparation of the double fluoride salt involves the reduction of U(VI) to U(IV) by SO_2 in the presence of formic acid and the simultaneous conversion of U(IV) to insoluble $UF_4 \cdot NH_4F$ by the addition of NH_4F to the system. It is thought that the reduction of U(VI) to U(IV) proceeds by the action of hyposulfurous acid produced by reduction of sulfurous acid with formic acid. Recommended conditions for the production of the double fluoride salt are: temperature, 90°C; *p*H of solution, 1 to 2; formic acid, 2.5 times stoichiometric requirement; ammonium fluoride, 1.2 times stoichiometric requirement; uranium concentration, 25 g of uranium per liter; reaction time, 90 min; and SO_2 flow rate, 1.5 liters/min.

The double fluoride salt may be converted to a completely anhydrous material by drying at 110°C. On heating the salt in an atmosphere of nitrogen, ammonium fluoride is evolved and UF_4 powder (6- to 10-μ particle size) is produced. At 300°C the decomposition reaction is first order with respect to the concentration of NH_4F remaining in the solid. An activation energy of 13.5 kcal/mole was calculated for the reaction.[2]

Muir has published[3] the results of a comprehensive study of the preparation of $UF_4 \cdot NH_4F$ from uranyl nitrate solutions. Kinetic studies on the production of $UF_4 \cdot NH_4F$ indicated that (1) the maximum rate of reaction is obtained at about 88°C, (2) it should be possible to increase the rate of reaction at a higher temperature in a pressurized system, (3) the rate of reaction is increased over a considerable range by an increase in the quantity of formic acid initially added to the system, (4) the hydrogen-ion concentration has a definite effect on the rate of reaction and should be maintained at as low a level as possible, and (5) since it appears that the active reducing agent is continuously regenerated in the system, it may be practical to recycle the barren solution to initiate further reduction of additional batches of uranium.

At the USAEC Feed Materials Production Center, Fernald, Ohio (operated by National Lead Co. of Ohio, NLCO), purified uranium trioxide is converted to uranium tetrafluoride, which is subsequently reduced to massive metal and then fabricated into fuel cores. Each process step generates uranium-bearing residues that must be processed for uranium recovery either by direct remelting or by hydrometallurgical techniques.

Low-grade residues are processed for uranium recovery by a HCl leach and precipitation of uranium

as uranyl ammonium phosphate (UAP). This material is then calcined and treated by the Winlo process to produce UF_4 suitable for recycle to the uranium-metal production process.[4,5] Basically, the Winlo process consists of three steps: (1) the preparation of a hydrochloric acid solution of uranium by the dissolution of calcined UAP or U_3O_8 in 30% HCl containing nitric acid as an oxidant, (2) the addition of hydrofluoric acid and cupric sulfate to the system, and (3) reduction of U(VI) to U(IV) and precipitation of UF_4 by the catalytic action of the cuprous chloride ion which is continuously regenerated by bubbling SO_2 through the solution at 90°C. A complete description of the Winlo process was presented in a previous issue of *Reactor Fuel Processing*.[6] Cavendish[5] has reviewed the operation of a plant-scale production unit at NLCO employing the Winlo process for the recovery of uranium waste materials and has summarized the results of tests evaluating the recyle of UF_4 to the refinery.

Uranium dioxide of high purity has been prepared[6a] directly from uranyl nitrate solutions by reduction with hydrogen at 300°C and 40 atm. The nature of the reaction was affected by the *p*H of the solution and by the molality of the uranyl nitrate solution. For solutions containing greater than 0.05*M* uranyl nitrate at a *p*H less than 2.7, the reduction reaction at 300°C proceeds by the direct formation of UO_2:

$$UO_2^{2+} + H_2 \rightarrow UO_2 + 2H^+$$

In more dilute solutions at a *p*H less than 2.7, the reaction proceeds by the formation of intermediate oxides:

$$UO_2^{2+} + 1.8H_2O \rightarrow UO_3 \cdot 0.8H_2O + 2H^+$$

$$UO_3 \cdot 0.8H_2O + 0.75H_2 \rightarrow UO_{2.25} + 1.55H_2O$$

$$UO_{2.25} + 0.25H_2 \rightarrow UO_2 + 0.25H_2O$$

The reactions in dilute solutions involve the precipitation of a solid phase which is then further reduced to UO_2. The rate of reduction of the solid precipitate is apparently controlled by the diffusion of oxygen ions. This was verified by the observation of a marked decrease in the reaction rate after the initial hour of reaction. At this time the hydrogen is consumed both by the reduction of the solid precipitate and by the reduction of nitrate ions.

Although the thermal decomposition of uranyl nitrate hexahydrate (UNH) is an important step in the production of UO_3, many uncertainties exist in the process performance owing to a lack of information on the decomposition of UNH. Ondrejcin[7] has investigated the thermal decomposition of UNH in the temperature range 250 to 400°C at atmospheric pressure and at pressures less than 0.1 mm Hg. A manuscript of this recently published paper was previously reviewed in this journal,[8] and therefore no details of this work will be presented here.

Brčić and associates[9,10] have investigated the reactions between hydrazine and uranium fluorides for possible application in the preparation and purification of uranium fuel materials. The reaction between gaseous UF_6 and N_2H_4 at 80°C was observed[9] to proceed with the formation of a white powder tentatively identified as $N_2H_5UF_6$ analogous to NH_4UF_6. In anhydrous hydrogen fluoride solvent, uranium hexafluoride reacts at 0°C with hydrazinium difluoride ($N_2H_6F_2$) to form a yellow solid, $N_2H_6UF_7$, hydrazinium heptafluorouranate(V).[10] When exposed to moist air or to reaction with water, the solid compound is reduced to hydrazinium pentafluorouranate(IV). Hydrazinium heptafluorouranate is thermally unstable. In an inert atmosphere the decomposition of $N_2H_6UF_7$ proceeds as follows:

$$N_2H_6UF_7 \xrightarrow{70°C} N_2H_6UF_6 + UF_4 \xrightarrow{180-200°C}$$

$$N_2H_5UF_5 + UF_4 \xrightarrow{310°C} 3UF_4 \cdot HF \xrightarrow{380°C} UF_4$$

Hydrazine complexes with uranyl fluoride have been prepared by Sahoo and Satapathy.[11] The complex $UO_2F_2(N_2H_4HF)_3 \cdot 1.5\ H_2O$, when heated in vacuum at 200°C, decomposes to $UF_4N_2H_4HF \cdot H_2O$ which, in turn, when the temperature is raised to 400°C, decomposes further to yield anhydrous UF_4. Uranyl fluoride forms another complex compound with hydrazine, $UO_2F_2(N_2H_42HF) \cdot 1.25\ H_2O$. This material, when heated in vacuum, yields directly anhydrous uranium tetrafluoride.

Production of Uranium Compounds by Gas–Solid Reactions

Gas–solid reactions, particularly the reduction of uranium trioxide with hydrogen and the hydrofluorination of uranium dioxide to produce uranium tetrafluoride, are important steps in the production of both uranium metal and uranium hexafluoride. The rate of these reactions is determined by the structure of the solid surface that is continuously modified throughout the reaction. Because thermal damage of the solid surface is significant in this type of heterogeneous reaction, considerable attention has been directed toward using fluid-bed reactors in the production of uranium feed materials. Fluid-bed reactors offer the advantage of efficient gas–solid contact and temperature control.

In 1964 the American Institute of Chemical Engineers sponsored a symposium on nuclear plant experience with fluidized beds. The papers presented at the symposium have been published as a separate volume in the *Chemical Engineering Progress Symposium Series*.[12] Most of these papers were previously reviewed in *Reactor Fuel Processing*.[13]

A patent has been issued to Levey[14] on a method for operating a fluidized bed in the processing of uranium feed materials that are not capable of being processed in ordinary fluid beds owing to very coarse or very fine particle sizes of the feed materials. The method involves imposing a large pulse flow of gas on the system such that the height of the expanded bed oscillates between 10 to 100% above the settled bed height. Use of this technique gave gas flow rates five times that available in conventional steady flow systems, and therefore the time required for conversion of, for example, U_3O_8 to UF_4 was significantly reduced.

The reaction of uranium compounds with gaseous fluorine is an important step in the production of UF_6 for isotope separation in the gaseous diffusion plant. All uranium, whether destined directly for ^{235}U production or for nuclear reactors, is eventually processed in a gaseous diffusion plant and must be converted to UF_6. Oxides prepared from virgin ore and uranium returned from plutonium-production reactors and from power reactors are processed in this manner. Also, valuable uranium is recovered as UF_6 from waste streams. Smiley and associates[15] have reviewed the role of fluorine in uranium-processing operations with specific emphasis on the description of equipment employed in these operations.

The reduction of UO_3 to UO_2 by hydrogen has been studied as a continuous operation in a stirred-bed reactor.[16] In this reactor (Fig. V-1), which is 2 in. in diameter, the agitation of the solids was provided by a screw-flight rotor. The reactor was operated with countercurrent solids and gas flows. It was observed that neither stirrer agitation nor gas motion exerted a major influence on the reaction rate. In tests performed with UO_3 feed activated by hydration, conversions to 99% UO_2 were achieved at 530°C in pure hydrogen with residence times as short as 12 min. For UO_3 derived from fluid-bed denitration of UNH, residence times of approximately 1 hr at temperatures of 580°C were required to achieve complete reduction to UO_2.

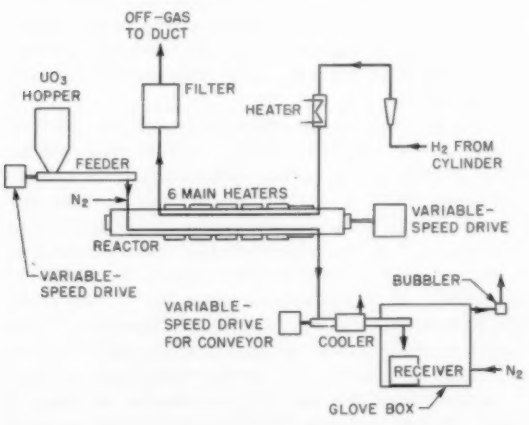

Fig. V-1 Schematic diagram of apparatus for reduction of uranium trioxide.[16] From Transactions of the Institution of Chemical Engineers (London), *44(3): T97 (1966).*

Uranium dioxide has been hydrofluorinated[17] in the continuous stirred-bed reactor (Fig. V-1) at a temperature of 450°C yielding a UF_4 product containing 0.01 wt.% UO_2 and with less than 0.5 vol.% HF remaining in the off-gas. The reaction was shown to proceed rapidly to 95% conversion, whereupon the reaction follows first-order kinetics with respect to the remaining UO_2 content down to values as low as 0.01 wt.%. The apparent activation energy calculated from experimental data obtained from tests in the stirred-bed reactor was 9.5 kcal/mole. Reaction rates obtained in this equipment were notably higher than those found in other types of reactors such as fluidized beds. The absence of diffusional resistance in the gas phase indicates that contact between solids and gas in the stirred-bed system is excellent. Stirred-bed reactors appear to be well suited to continuous processes where extended or well-defined residence times are required and where high levels of conversion are desired in either the solid or the gas phase.

Production of Plutonium Metal

Plutonium metal is normally produced by the bomb reduction of a plutonium compound by an active metal in a sealed pressure vessel. The procedure adopted at Rocky Flats involves the reduction of PuF_4 by calcium metal. A mixture of PuF_4 and calcium metal is placed within the reduction vessel, and the vessel is heated in an induction furnace until the reaction is initiated. Conner[18] has observed that the degree to which the calcium and PuF_4 reactants are mixed does not affect the reduction yield. The location of the PuF_4 within the reduction vessel does, however, affect reduction yield. High metal yield can be obtained from an unmixed charge if the PuF_4 is placed on top of the calcium. If the PuF_4 is placed at the bottom of the vessel, the metal yield is poor.

Plutonium metal yield was found[19] to be directly proportional to the fluoride content of the PuF_4 and inversely proportional to the plutonium content of the PuF_4. Metal yield is adversely affected if the PuF_4 contains more than 1% sulfate.

Electroreduction Processes

A method for producing plutonium metal from PuO_2 by electrolysis in molten fluoride salts has been developed at Savannah River Laboratory.[20] Electrolytes containing 50 wt.% LiF, 20 wt.% BaF_2, and 30 wt.% PuF_3 gave the best cell performance. A maximum production rate of 40 g of plutonium metal

per hour was achieved in a laboratory-scale cell which consisted of a tantalum crucible, $2\frac{5}{8}$ in. in diameter and $5\frac{1}{2}$ in. tall (Fig. V-2). The crucible served as the cathode. The anode was constructed of graphite and consisted of a flat disk, $\frac{1}{4}$ in. thick and $1\frac{1}{4}$ in. in diameter, attached to a riser rod. Incorporation of this design made it possible to promote mixing of the electrolyte melt by the gases evolved

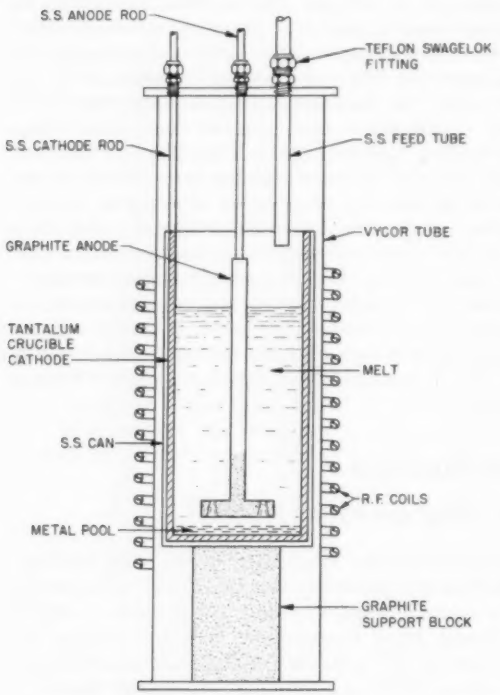

Fig. V-2 Electrowinning cell assembly.[20]

from the anode during cell operation. The cell was operated at 1000°C at a current of 100 amp. Plutonium dioxide was added at a controlled rate to the melt, and molten metal was deposited in a pool at the bottom of the crucible. Under these conditions, utilization of PuO_2 was essentially 100%. Current efficiencies of 10 to 20% were usually achieved.

The purity of the metal product was identical to that obtained by bomb-reduction techniques, with the exception that the product usually contained 3500 ppm tantalum derived from the crucible.

The following conditions were found to be significant for the electrowinning of plutonium metal from fluoride melts: (1) low anode current density (<1 amp/cm^2) to avoid the anode effect; (2) high cathode current density (>1 amp/cm^2) to favor metal production over cyclic oxidation–reduction between several plutonium oxidation states; (3) maintenance of a cathodic potential on the reduced metal to prevent loss by reaction with the electrolyte; and (4) a low, uniform rate for addition of the PuO_2 feed to ensure the complete assimilation of the PuO_2 into the system.

A program to demonstrate the continuous production of plutonium metal by electroreduction from a fused chloride salt is under way at Hanford Atomic Products Operation (HAPO).[21] The process involves feeding of $PuCl_3$ into a melt consisting of 28 wt.% $BaCl_2$, 42 wt.% KCl, and 30 wt.% $PuCl_3$ and electrodepositing molten plutonium at 800°C. A detailed description of the process and equipment was presented in a previous issue of *Reactor Fuel Processing*.[22] Recent work[21] has concerned the design, fabrication, and operating behavior of ceramic cells for the electroreduction process. Ceramic components constructed from 6 mole % Mg_2TiO_4 and 94 mole % MgO have operated successfully in demonstration tests and appear to offer satisfactory corrosion resistance.

Production of Plutonium Compounds from Plutonium Dioxide

A process for the preparation of metallic plutonium using a chloride intermediate is being developed at HAPO. The proposed process includes calcination of plutonium nitrate to PuO_2, chlorination of PuO_2 to $PuCl_3$, and electrolytic reduction of $PuCl_3$ to plutonium metal. Fullam and Soine[23] have evaluated the direct calcination of plutonium nitrate solution to oxide with specific emphasis on the reactivity of the powder toward chlorination. Calcination was carried out in an electrically heated screw reactor, 2 in. wide, 3 in. deep, and 36 in. long. Plutonium nitrate solution enters the reactor and forms a pool in the trough of the calciner. As the liquid moves down the calciner, evaporation and decomposition occur and a slurry forms. Continued heating converts the slurry to a dry powder that is discharged from the reactor. The calciner is operated at a temperature between 400 and 450°C.

Tests to evaluate the chlorination of the calciner product were carried out in a stirred-bed reactor using phosgene and carbon tetrachloride as chlorinating agents.[23] A description of this system appeared in the Summer 1966 issue of *Reactor Fuel Processing*.[24] It was observed that the reaction rate increases with increasing temperature up to 500°C, whereupon, at temperatures above 500°C, the reaction rate and the extent of conversion decrease.[23] The optimum chlorination temperatures appear to be in the range of 450 to 500°C. It was found that, in order to achieve greater than 77% conversion of PuO_2 to $PuCl_3$, it was necessary to add an activating agent to the calciner nitrate feed. By adding ammonium sulfate to the feed (molar ratio SO_4^{2-}/Pu of 0.3), a highly reactive PuO_2 was produced; conversions to $PuCl_3$ as

high as 97% were obtained. The reactivity of the PuO_2 product was also affected by the calcination temperature and the residence time. Generally, increased temperature and residence time led to decreased oxide reactivity. However, if the temperature was too low or the residence time was too short, the presence of volatile materials in the oxide caused a reduction in oxide reactivity.

A continuous gas–solids contactor that offers the advantages of safe geometry, high throughput, and simple operation has been described by Fullam.[25] This unit has been evaluated for the conversion of PuO_2 to PuF_4 by reaction with HF. The body of the contactor consists of a hollow, cylindrical slab that is divided into an upper and lower section by a porous plate (see Fig. V-3). The solids enter the upper section of the reactor at the periphery and are moved in the center by a rabble arm. The rabble arm is a rotating rake with pitched teeth which move the solids in a spiral path from the wall to the center, whereupon the solids leave the contactor through a downcomer pipe. The porous plate serves as a support for the solids and as a gas distributor.

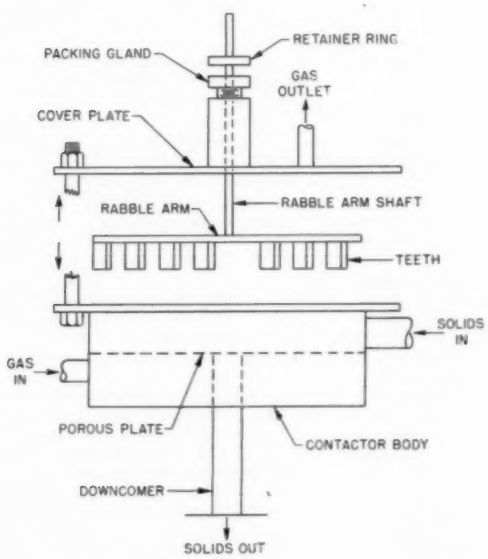

Fig. V-3 Contactor for conversion of PuO_2 to PuF_4 (expanded view).[25]

The hydrofluorination of PuO_2 was carried out in the contactor using two types of PuO_2: (1) oxide produced in a screw calciner by direct calcination of plutonium nitrate solution and (2) oxide produced by calcination of plutonium oxalate. Hydrofluorination was carried out for 2 to 3 hr at 500 to 600°C using undiluted HF. The results of these tests (Table V-1) show that (1) an activating agent such as ammonium sulfate must be added to directly calcined oxide to obtain adequate conversion; (2) directly calcined oxide containing ammonium sulfate can be adequately fluorinated at 500°C, but a temperature of 600°C is required to remove the sulfate from the fluoride product; (3) directly calcined oxide containing calcium nitrate can be readily hydrofluorinated at 500°C; and (4) oxide containing calcium nitrate shows a slightly higher reactivity toward HF than oxide derived from plutonium oxalate.

Thorium

The present position of thorium in the field of power reactors is in the nature of a reserve material. However, considerable technology on thorium chemistry and metallurgy is already available to meet any future production demands. Three recent publications[26–28] summarize the current status of thorium technology with specific emphasis on the utilization of thorium in power reactors.

A development program has been under way at Argonne National Laboratory to evaluate the reduction of thorium dioxide by zinc–magnesium alloys in the presence of molten fluxes.[29] In small-scale demonstration experiments, over 99% reduction of ThO_2 to metal was achieved in 4 hr with product purities up to 99.7%. A description of the process was presented in a previous issue of *Reactor Fuel Processing*.[30]

Thorium Dioxide

Interest in the use of thorium in power reactors has resulted in a considerable amount of process development work on methods for producing thorium oxide and mixtures of uranium oxide and thorium oxide. Workers at Oak Ridge National Laboratory[31,32] have developed a sol-gel process for producing dense spherical particles of ThO_2 which are suitable for vibratory compaction into tubes. Details of this

Table V-1 HYDROFLUORINATION OF PLUTONIUM OXIDE[25]

Feed material	Reactor temp., °C	Rabble arm speed, rpm	Feed rate, g of Pu/hr	Holdup, g of Pu	Residence time, min	Conversion, %*
Oxide from oxalate	500	12	280	795	170	88
Directly calcined oxide (no additive)	500	12	240	690	173	71
Directly calcined oxide [$(NH_4)_2SO_4$ added]	600	15	400	910	138	86
Directly calcined oxide [$Ca(NO_3)_2$ added]	500	15	390	770	118	92.5

*Conversion based on fluoride analysis of product.

process have already been described in *Reactor Fuel Processing*.[33] The use of a d-c arc plasma generator for the preparation of thoria microspheres in the size range 5 to 44 μ is being investigated at the Paducah Gaseous Diffusion Plant.[34] Kinoshita and associates[35,36] have studied a method for producing thoria based on the precipitation and calcination of thorium oxalate. The studies primarily concerned the investigation of the effects of processing conditions on the properties of the ThO_2 product and the effect of powder properties on the sintering of ThO_2. Two recent publications[37,38] discuss the sintering properties of UO_2-ThO_2.

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